COAL TAR DISTILLATION

A. R. WARNES

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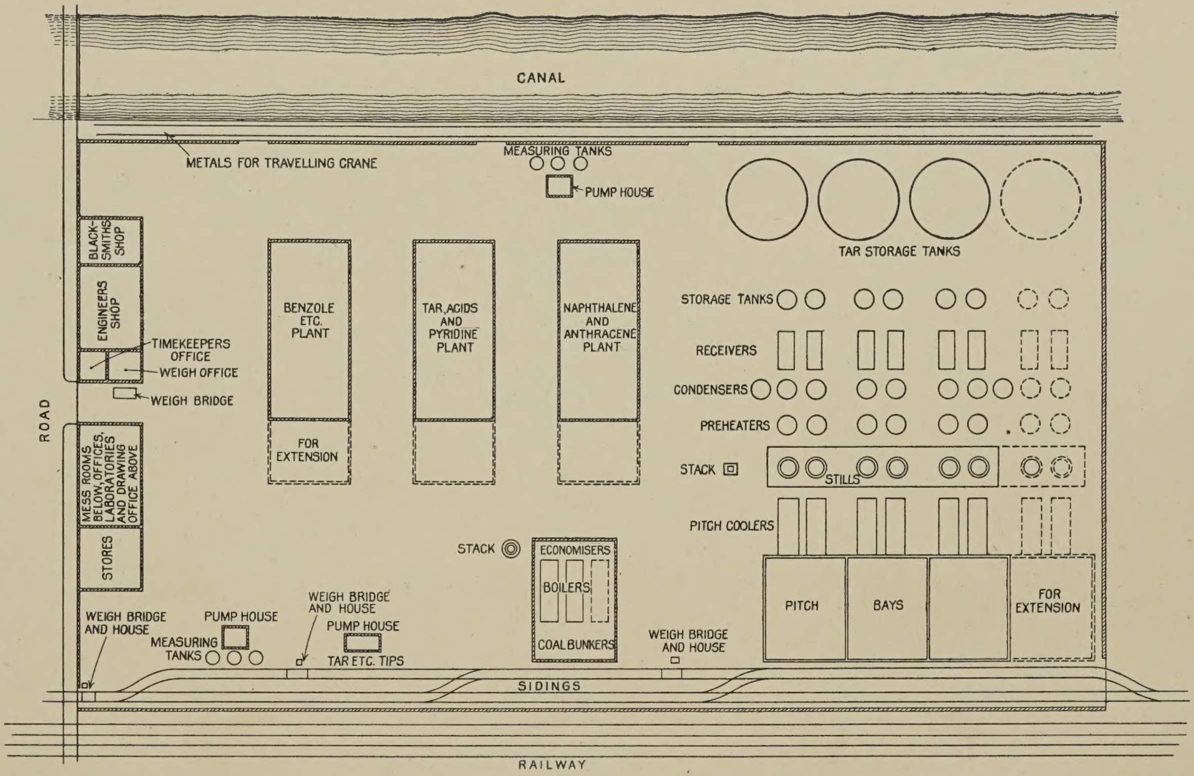

LAY-OUT OF TAR DISTILLERY ON AN IDEAL SITE

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COAL TAR DISTILLATION
AND
WORKING UP OF TAR PRODUCTS

BY

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ETC.

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THIS BOOK IS DEDICATED

TO

MY TEACHER AND FRIEND

DR. F. M. PERKIN, C.B.E., F.I.C.

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PREFACE TO THE THIRD EDITION

In preparing the third edition of this work the author has added a chapter dealing with the geology of coal, and also one on the constitution of coal, because he thinks it necessary that students, and others who are interested in coal tar, should have at least a general knowledge of the substance from which it is derived. A new chapter has been included which deals briefly with the lay-out of works, and several diagrams of ideal sites are used to illustrate the text; in doing this the author wishes it to be understood that ideal sites are very rarely met with, but that it is wise to seek for a position as near as possible to the ideal, and arrange the plant in the most efficient manner afterwards. The old Chapter I, now Chapter III, has been revised considerably, and the formation and constitution of coal tar has received some attention. Additions have been made to many of the other chapters, and the one dealing with tar works tests has been considerably enlarged. A brief Bibliography has been placed at the end of several of the chapters.

The author has to thank the many manufacturers who have been kind enough to supply details of their special plants and lend him blocks or drawings with which to illustrate the text. He also has again to express his best thanks to his friend, Mr. Arnold R. Tankard, F.I.C., for his help and criticisms upon some of the chapters. Thanks are due to Dr. M. C. Stopes and the Controller of His Majesty's Stationery Office for permission to use the microphotographs which illustrate Chapter II. These microphotographs are reproduced from Stopes and Wheeler's *Monograph on the Constitution of Coal.* For help during the earlier periods in the preparation of this work the author has to thank his assistant, Miss O. M. Sanderson, F.C.S. He is also indebted to Mr. Burnard Geen, M.Inst.C.E., and to Mr. J. E. Blundell, Engineer of the Carlisle Gas Works, for their kindness in allowing a description of the concrete tanks erected at the Carlisle Gas Works to appear in Chapter V, and also for the use of the photographs and drawing illustrating this description. For permission to publish the specifications on pages 388, 397, 431 the author has to thank the Committee of the British Engineering Standards Association, and appreciation of the joint kindness of Dr. H. G. Colman and the Publication Committee of the Society of Chemical Industry for allowing the full text of Colman and Yeoman's paper on the *Determination of Benzene, Toluene, etc., in Coal Tar and Similar Products* to appear in the analytical chapter, is expressed in this place.

In the revising of the Index and making many additions thereto, and for much other valuable assistance, the author takes this opportunity of recording his best thanks to his wife.

To the publishers, he expresses appreciation of their kindly forbearance in regard to the long delay which has occurred during the preparation of this edition owing to many unforeseen circumstances.

ARTHUR R. WARNES.

HULL, *October*, 1923.

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COAL TAR DISTILLATION AND WORKING UP OF COAL TAR PRODUCTS

CHAPTER I

COAL

As coal is the mother substance from which coal tar is obtained it is desirable, especially from the point of view of the student, to consider briefly the subject of its geology, origin, and constitution before dealing with the chief theme of this book: coal tar and its distillates.

It is not a very easy matter to give a simple definition of the term coal, those such as "mineralised vegetation" and "bottled-up sunshine" are very unsatisfactory and misleading. The most suitable definition is that given by Stopes and Wheeler,[1] which is as follows: "Ordinary coal is a compact, stratified mass of 'mummified' plants (which have in part suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter. Veins, partings, etc., which are found in nearly all coals, are local impurities and are not part of the coal itself."

Coal is found in many parts of the world, and occurs in the sedimentary rocks of the Palæozoic, Mesozoic, and Caïnozoic eras. In the Palæozoic periods coal is found in the Devonian, Carboniferous, and the Permian, the coal measures epoch of the Carboniferous period yielding enormous quantities of coal. These deposits are worked in Great Britain, Australia, India, South Africa, France, Germany, and North and South America. In the three periods of the Mesozoic era, the Triassic, Jurassic, and Cretaceous, deposits of coal are found in Europe, Russia, Japan, and North America, and the Oligocene and Miocene periods of the Cainozoic era yield coal in the deposits in Britain, Europe, Russia, United States, and Japan. For the benefit of the non-geological reader the following table is given, in which is shown the order of succession of the geological eras, as affects this subject.

By far the largest deposits of coal (chiefly humic or so-called bituminous) occur in the coal measures of the Carboniferous period. These deposits consist of an alternation of layers, varying in thickness, of shales, coal, clays, and sandstones. The depth of the layers or seams of coal vary from a few inches to many feet, and the total thickness of the strata amounts to many thousands of feet; for instance, the strata of some portions of the coal basin of South Wales is upwards of 10,000 feet thick.

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[1] See monograph on the Constitution of Coal. H.M. Stationery Office.

As indicated by the definition given at the beginning of this chapter, coal is derived from vegetable matter, and as the huge deposits of coal in the world must have required vast quantities of plant material for their formation, it is necessary for us to consider how these accumulated. Differences of opinion still exist between some authorities upon this subject, but these are being gradually cleared up by careful research, and the great majority of workers on this important problem are inclined to view the matter much in the same way as Stopes and Wheeler. Their line of thought in this direction is admirably shown in tabular form as follows :—

TABLE I

Era.	Period.	
Quaternary	Recent	Peat.
Cainozoic or Tertiary	Pliocene	
	Miocene	Coal, chiefly brown coal and lignite, found in England, U.S.A., Japan, Germany, Hungary, Russia, India, and Greenland.
	Oligocene	
	Eocene	
Mesozoic or Secondary	Cretaceous	Coal, lignitic, found in Alaska and Rocky Mountain region.
	Jurassic	Coal, found in Britain, Hungary, Russia, and Japan.
	Triassic	Coal, found in Japan.
Palæozoic or Primary	Permian	Coal, found in France, Saxony, and Bohemia.
	Carboniferous	Coal, chiefly bituminous, found in Britain, India, Australia, South Africa, U.S.A., France, Germany, Brazil, Chili, Argentine, etc.
	Devonian—	
	Upper	Coal, bituminous, found in the Polar regions.
	Middle	
	Lower	
	Silurian	
	Ordovician	
	Cambrian—	
	Upper	
	Middle	
	Lower	

THE LEADING MODES OF ACCUMULATION OF COAL-FORMING VEGETABLE MATERIAL[1]

A. In Sea Water

(i) *Drifted land material*, which may travel far, settling water-logged beyond the reach of mineral detritus.

This would principally be :—

(*a*) Tree trunks and logs, which may accumulate in large quantities.
(*b*) "Floating islands" of various plants growing entangled together, generally very local.

(ii) *Fucoid algæ*, forming a shore accumulation (only one instance of a coal so formed is known, from Russia).

B. In Brackish Water

(i) *In situ* material, the droppings of coastal forests or mangrove-like swamps.
(ii) *In situ* lowly swamp or bog plants.
(iii) Partly *in situ* and partly drifted from short distances in swamps.
(iv) B i, ii, iii, and A i (*a*), i (*b*), mingled in any proportion.

C. In Fresh Water

(1) In undisturbed lakes :—
  (*a*) From the gross debris drifted in from neighbouring forests.
  (*b*) The pure "plankton" or microscopic life of the lake.
  (*c*) *b*, mixed with only the spores, pollen, and finer ultimate debris of higher plants.
  (*d*) Plants growing *in situ*, reeds, etc.
  (*e*) *a*, *b*, and *c*, mingled, or layered, in any proportion, may be layered with *d* as the water-level changes.

(ii) In estuaries, river bends, and deltas :—
  (*a*) Drifted material which may have travelled far ; nearly all wood.
  (*b*) Drifted material from near at hand, therefore including soft leaves etc., as well as wood.
  (*c*) Floating islands.
  (*d*) Swamp or bog plants, *in situ* growths.
  (*e*) *a*, *b*, *c*, and *d*, mingled in all possible proportions.

(iii) In swamps formed over large areas, interspersed with lakes, *in situ* and drift material mingled.

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[1] See monograph on the Constitution of Coal. H.M. Stationery Office.

D. On Land

(i) Highland moors of various types, "mosses," etc., moor-peats.
(ii) Moorland peat and forest, mingled or alternating.
(iii) Swamp peats—these merge with C iii.
(iv) Dry forest floor accumulations.

For the production of what Stopes and Wheeler term major coal-fields, "changes of the surface level of the land successively repeating the favourable conditions for accumulation were necessary. Major coal-fields appear generally to have been formed under conditions B iv or C iii ; but may have been formed under B i, ii, iii, or iv, C i or ii, or others, but could *never* have been formed by A i, ii, C i*b*, C i*c*, C ii*c*, or D iv. These latter, and, indeed, all the modes of accumulation outlined above, may form minor coal-fields as well as isolated seams."

In order to give the reader some idea of the formation of a coal seam we will consider briefly what appears to have taken place during the Carboniferous period, in the deposits of which the greatest amounts of coal are now found. Geological researches indicate that this period was one of comparative quiescence, one in which terrestrial disturbances were at the very lowest. During this state geographical change was very slow indeed, and this would account for great uniformity of life, a condition which is borne out by the persistence of the same types of plant and animal fossils found in the deposits of this period. Those agencies which bring about change in land surfaces were able to prolong their course of action, and thus vast deposits of sandstones, limestones, shales, etc., were formed ; a very gradual levelling up of the land surface and a shallowing of the existing seas taking place. Eventually these conditions produced large tracts of low-lying land subject to inundation, which became covered with a growth of luxuriant plants. Thus commenced the coal measures epoch. Huge swamps were formed, in many cases inland and intersected by slowly running water-ways and in others in estuarine positions.

Under the suitable climatic conditions then existing vegetation grew at a rapid rate and continued to flourish for very considerable periods, quantities of it dying and falling into the shallow water from time to time. Under the water this dead vegetation suffered partial decomposition and became a more or less compact mass upon which new plant life sprang up. This in its turn died, and so the process was repeated many times over. In cases of swamps intersected by water-ways or existing in an estuarine position, much floating vegetable debris was collected by the partially exposed roots of the larger plants and the tangled mass of the smaller types of vegetation. Eventually a pulpy mass of partly decomposed vegetable matter accumulated to a thickness of between 50 to 100 feet, or more. During this period the land was very, very slowly sinking, and this subsidence eventually becoming more rapid the area became covered with water too deep to allow of the existence of vegetable life. At this stage mud and fine sand were brought along and deposited over the compact mass of vegetable matter, either by running water or by marine agency, and this process went on for a considerable period, during which the land continued to sink. Eventually a time arrived when the subsidence ceased altogether, or the sedimentary matter was being deposited at a greater rate than the sinking of the land, shallow lakes or seas were then formed, plant life began to reappear, first at the water edges and then to gradually creep towards the centre until the whole of the area of water became covered with vegetation. At the present state of geological knowledge it seems that by many repetitions of the processes just described the coal measures, with their large number of seams of coal and layers of sandstone and shale, were laid down.

The following diagrams, produced by Prof. Bone,[1] are of particular interest at this point.

The whole process of coal formation, so far as it is known to-day, may perhaps best be epitomised in some such provisional diagram as the following :—

OUTLINE OF COAL FORMATION

(0)

Original material.

- Lignocelluloses.
- Vegetable proteins.
- Resins.

(1)

(*a*)	(*b*)	(*c*)
FERMENTATION in peat bog with evolution of gases.	MACERATION by water and possibly also SEGRATION INTO :— (*a*) Colloidal solution (gels). (*b*) Insoluble matter.	TRANSPORTATION by water and RE-DEPOSITION elsewhere.

(2)

(*a*)	(*b*)
BLANKETING under newer strata and CONSOLIDATING and DE-WATERING of Mass by Pressure.	EARTH MOVEMENTS producing LAMINATED STRUCTURE.

(3)

BITUMENISATION UNDER PRESSURE AND SLOWLY INCREASING TEMPERATURE

(*a*) Progressive De-watering.
(*b*) Loss of CO_2 and H_2O (Cellulosic Condensation).
(*c*) Amalgamation of Cellulosic (Humic) and Protein Matter
(Pressure—Distillation).

It would thus appear that brown coals and lignites may be regarded as intermediate products between peat and bituminous coals.

---

[1] "Brown Coals and Lignites," Prof. W. A. Bone, F.R.S., Cantor Lectures, *Jour. Royal Society of Arts*, No. 3662, 26.1.23, p. 175.

THE WOOD TO COAL SERIES[1]

0. Woody Tissue (Lignocelluloses)		↓
↓		↓
1. Peat (Quaternary)	Water = 90 Combustible = 10	↓
↓		↓
2. Earthy brown coals (Tertiary)	Water = 40 to 50 Coal = 50 to 60	Woody brown coals (Tertiary)
↓		
3. Laminated Lignites (Chiefly Tertiary)	Water = 20 to 40 Coal = 60 to 80	
↓		
4. Sub-Bituminous Coals (Chiefly Cretaceous	Water = 10 to 20 Coal = 80 to 90	
↓		
5. Bituminous coals (Mesozoic Carboniferous)	Water <10 Coal >90	
↓		
6. Semi-Bituminous Coals (Carboniferous)		
? ↓ ?		
7. Anthracitic Coals (Carboniferous)		

From the careful researches of many eminent geologists and palæo-botanists we learn that coal was formed from a number of species of plants occurring in the following groups :—

A. Thallophyta.
B. Bryophyta.
C. Pteridophyta.
D. Gymnospermæ.

Groups A, B, and C belong to the Cryptogamic or lower division, and Group D to the Phanerogamic or higher division of the plant kingdom.

In Group A (Thallophyta) occur the algæ and the fungi, and these cellular Cryptogams, owing to their delicate structure, are not well adapted to be preserved in the fossil condition. On this account the absence of many classes of Thallophytes in coal seams is no ground for concluding that they did not exist during the periods when these were in the stages of formation. That some types of coal were formed wholly or partly from algæ is still an unsettled problem ; Bertrand and Renault consider that some Boghead coals were formed almost entirely from the remains of a gelatinous alga, which they called *Pila bibractensis*.

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[1] "Brown Coals and Lignites," Prof. W. A. Bone, F.R.S., Cantor Lectures, *Jour. Royal Society of Arts*, No. 3662, 26.1.23, p. 174.

Fossils of the lower fungi (Bacteria) and of the higher fungi (Ascomycetes) have been found in the strata of the Carboniferous period, and it is most likely that these lowly forms of plant life assisted in the partial decomposition of the higher plants during the initial stages of coal formation.

Under Group B (Bryophyta) are placed the mosses (Musci), which, when associated with other types of vegetation growing in a water-logged soil, form peat bogs, and it is quite probable that some of the brown coals of the Tertiary (Cainozoic) era were formed from peat.

The plants of Group C (Pteridophyta) during the Carboniferous period formed the greater quantity of the land vegetation, and in this period they were at the stage of highest development. Quite a large number of species of ferns (Filicinæ) occur in the strata of the Carboniferous period, and fossils of the fronds of many species are very frequently found. In the British coal measures the most abundant species are : Pecopteris and Alethopteris. In the class of the Equisetinæ the order Calamarieæ was abundantly represented, and some of these plants, which were like the horse-tail of our present-day ponds and swamps, grew to a height of 90 feet. Of the Lycopodinæ the two great extinct orders, the Sigillarieæ and the Lepidodendreæ, were abundantly represented. Plants of both these orders grew to large dimensions. Lyell, in his *Elements of Geology*, records the finding at Newcastle of a specimen of Sigillaria 72 feet in height. Fossils of Lepidodendron have been found, which when living were between 30 and 40 feet high.

A small class of plants, the Sphenophyllinæ, added its quota to the formation of coal, and it is of special interest to botanists and palæo-botanists, as it occupies an intermediate position between the Lycopodinæ and the Equisetinæ.

Group D (Gymnosperms) is one of considerable interest, as it includes species of conifers (pine trees), very closely allied to those of the present day. The lowest coniferæ (family Araucarieæ) were apparently the most prevalent, and evidence that plants of the genus Pinus, which flourishes abundantly to-day, also formed part of the coal-producing flora exists in the fact that seed-cones of these trees have been found in coal deposits.

The family Cordaiteæ is most richly represented in the carboniferous deposits, and on account of their fossil remains being in such an excellent state of preservation the morphology of this genus is almost as well known as that of the gymnosperms existing to-day. These plants, when fully grown, were of considerable height and bore spikes of unisexual flowers.

Other plants in this group, the remains of which are found in coal-bearing strata, are those of the families Cycadaceæ and Ginkgoaceæ, but these are far less common than those mentioned above.

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CHAPTER II

CLASSIFICATION AND CONSTITUTION OF COAL

Coals vary very much in character, and this makes it convenient to divide them broadly into the following groups :—

1. Brown Coals or Lignites.
2. Sapropelic Coals { Cannel Coals. / Bogheads or Torbanites.
3. Humic or Bituminous Coals.
4. Anthracite Coals.

From a geological point of view the brown coals are considered to be of comparatively recent origin, but it is not possible to draw a hard-and-fast line in this matter as coals of this description are found not only in the Cainozoic (Tertiary) era, but in the Cretaceous period of the Mesozoic era (Spain, N.W. America, and Vancouver). The same may be said of the other types of coal ; for instance, bituminous coals are usually found in the coal measures of the Carboniferous period (Palæozoic), and yet coal of this kind occurs in the deposits of the Cainozoic (Tertiary) era ; for example, that of the famous Miike mine in Japan. Again, semi-anthracitic coal is found in the Lias of the Jurassic period (Mesozoic era), in Hungary, when it usually occurs in the deposits of the Carboniferous period.

The appearance and structure of the lignites vary very much. In some kinds there is a considerable quantity of what appears to be wood very little altered in form or structure ; there are also fragments of bark and leaves, and the remainder of the coal is practically structureless. Other varieties are very fibrous and loose, and others are compact and contain earthy matter. Brown coals, on the other hand, show little or no woody structure, are more compact, and are as the name indicates, of a brown colour.

The Sapropelic or Cannel and Boghead coals are very much alike in appearance. They are black or brown, dull of surface and, like anthracite, do not soil the hands. Also, they do not exhibit, except very occasionally, any definite vegetable structure. When broken they both show a conchoidal fracture.

Bituminous coals are black, and are either of a more or less even brightness or of a mixture of dull and bright layers. Veins of iron pyrites or of other minerals often show themselves in the joint faces, and when these coals are broken they generally separate into rectangular pieces.

The Anthracite coals are very hard, are black or brownish, and they have a more or less metallic lustre. When broken they show a conchoidal fracture, which is characteristic. When handled they do not soil the fingers.

Various schemes for the classification of coals based upon analytical results have been put forward from time to time, but not one of them answers the purpose from all points of view. The tables given below will give the reader some idea of the methods used.

TABLE 2

FIELD'S CLASSIFICATION

Kind of Coal	Containing least Carbon			Containing most Carbon			General Average			
	Volatile	Carbon	Ash	Volatile	Carbon	Ash	No. of Specimens	Volatile	Carbon	Ash
Bituminous	31·87	63·63	4·50	10·31	87·69	2·00	57	21·55	75·34	3·11
Semi-Bituminous ..	34·28	61·78	3·94	10·00	88·50	1·50	63	21·40	74·66	3·94
Partially Bituminous	33·80	61·26	4·94	10·00	88·13	1·87	17	20·43	76·12	3·45
Anthracitous	14·26	82·99	2·75	6·14	92·11	1·75	17	9·24	88·41	2·35
Anthracite	9·00	81·00	10·00	2·18	95·69	1·50	21	7·24	90·12	2·64

The late Professor Lewes[1] made for progress in the classification of coals by suggesting that the coking or non-coking power of a coal will depend upon the preponderance, in the first case, of resin bodies and hydrocarbons, and, in the second case, of humus bodies and residuum (carbon). He gives the approximate composition of these bodies as follows :—

	Per cent. carbon.	Per cent. hydrogen.	Per cent. oxygen.
A. Residuum (carbon) . .	100	—	—
B. Humus bodies . . .	62	5	33
C. Resin bodies . . .	79	11	10
D. Hydrocarbons . . .	96	4	—

From these figures the approximate composition of a coking coal or non-coking coal can be worked out, as the following examples will show.

A coking coal in which resin bodies and hydrocarbons preponderate :—

3A+B+3C+3D.

		C	*H*	*O*
3A	=	300	—	—
B	=	62	5	33
3C	=	237	33	30
3D	=	288	12	—
		887	50	63

= Carbon 88·7 per cent.
Hydrogen 5·0 ,,
Oxygen 6·3 ,,

This represents a South Wales coking coal.

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[1] *The Carbonisation of Coal,* Vivian Byam Lewes. Benn Brothers, Ltd. London.

TABLE 3

GRUNER'S CLASSIFICATION

Class	Composition Per Cent			Specific Gravity	Calorific Power Calories	Evaporative Power	Percentage of coke left on distillation	Nature of Coke	Character of Coal
	Carbon	Hydrogen	Oxygen						
1. Dry coals, long flame	70 to 80	5·5 to 4·5	19·5 to 15	1·25	8,000 to 8,500	6·7 to 7·5	50 to 60	Powdery or slightly fritted	Burn with a long, smoky flame. Disintegrate on heating. Can be used in reverberating furnaces or as an inferior gas coal.
2. Fat coals, long flame	80 to 85	5·8 to 5·0	14·2 to 10	1·28 to 1·36	8,500 to 8,800	7·6 to 8·3	60 to 68	Caked, but very porous	Burn with a long, smoky flame. Soften on heating. Of chief value as gas-making coals.
3. Fat coals	84 to 89	5·0 to 5·5	11·0 to 5·5	1·30	8,800 to 9,300	8·4 to 9·2	68 to 74	Caked and fairly compact	Burn with less smoke and a more brilliant flame than the coals of Classes 1 and 2. Soften and cake together on heating. Used for coking, gas-making and smithy work.
4. Fat coals, short flame	88 to 91	4·5 to 5·5	6·5 to 5·5	1·30 to 1·35	9,300 to 9,600	9·2 to 10	74 to 82	Compact	Burn with a short, bright, slightly smoky flame. Cake on heating. The best coking coals.
5. Lean coals, Anthracite	90 to 93	4·5 to 4·0	5·5 to 3·0	1·35 to 1·40	9,200 to 9,500	9·0 to 9·5	82 to 90	Slightly fritted or powdery	Difficult to ignite. Burn with a short and nearly smokeless flame. Disintegrate on heating or cake slightly. Used for steam-raising and as house coals.

TABLE 4

SEYLER'S CLASSIFICATION

	Carbon per cent.	Over 93·3	93·3 to 91·2	91·2 to 89·0	89·0 to 87·0	87·0 to 84·0	84·0 to 80·0	80·0 to 75·0
Hydrogen per cent. over 5·8	Genus	Anthracitic	Carbonaceous	Bituminous			Lignitious	
	Per-bituminous	—	—	Meta-	Ortho-	Para-	Meta-	Ortho-
				Per-meta-bituminous	Per-ortho-bituminous	Per-para-bituminous	Per-lignitious	
5·0 to 5·8	Bituminous	—	Pseudo-bituminous	Meta-bituminous	Ortho-bituminous	Para-bituminous	Meta-lignitious	Ortho-lignitious
4·5 to 5·0	Semi-bituminous	—	Ortho-semi-bituminous	Sub-meta-bituminous	Sub-ortho-bituminous	Sub-para-bituminous	Sub-meta-lignitious	Sub-ortho-lignitious
4·0 to 4·5	Carbonaceous	Semi-anthracite	Ortho-carbonaceous	Pseudo-carbonaceous (sub-meta-bituminous)	Pseudo-carbonaceous (sub-ortho-bituminous)	Pseudo-carbonaceous (sub-para-bituminous)	—	—
Under 4·0	Anthracitic	Ortho-anthracitic	Sub-carbonaceous	Pseudo-anthracitic (sub-meta-bituminous)	Pseudo-anthracitic (sub-ortho-bituminous)	Pseudo-anthracitic (sub-para-bituminous)	—	—

A non-coking coal with excess of humus :—

A+2B+C+D.

		C	*H*	*O*
A	=	100	—	—
2B	=	124	10	66
C	=	79	11	10
D	=	96	4	—
		399	25	76

= Carbon 79·8 per cent.
Hydrogen 5·0 ,,
Oxygen 15·2 ,,

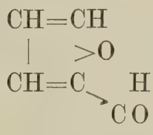
This represents a South Staffordshire coal.

The interested reader is referred to a very important paper dealing with the coking propensities of coal by Professor W. A. Bone, F.R.S., Mr. A. R. Pearson, M.SC., Mr. E. Sinkinson, B.SC., and Mr. W. E. Stockings, M.SC.[1]

In Chapter I it was explained that coal is derived from various species of plants, and as a preliminary to a concise survey of what is known of the constitution of coal, the substances which go to build up the plant structure or play some special part in its life-processes will be considered briefly. A plant is, broadly speaking, a mass of cells, the walls of which are constructed of cellulose and its derivatives, and these will be dealt with first as under :—

Cellulose $(C_6H_{10}O_5)n$. This material is not easily oxidised, and it offers considerable resistance to dilute alkaline oxidising agents, but when oxidation is brought about oxycelluloses and soluble products of low molecular weight (carbon dioxide and oxalic acid) are produced. When submitted to the action of specific micro-organisms cellulose is broken down chiefly into hydrogen, methane, carbon dioxide, and fatty acids. If subjected to temperatures above 250° C., the cellulose molecule is decomposed into a number of substances, the nature of the decompositions being extremely complex. Some of the materials formed are : Carbon monoxide and carbon dioxide, acetic acid, methyl alcohol, acetone, furfural or furfuraldehyde and tar, and charcoal.

The structural formula for furfural is :



$$\begin{array}{l} CH{=}CH \\ |\qquad >O \\ CH{=}C\searrow\ \ H \\ \qquad\quad CO \end{array}$$

Ligno-cellulose (probably $C_{24}H_{24}(CH_3)_2O_{10}$). A compound of cellulose and " lignone " (a group of ketone bodies). The presence of the lignone groups in the ligno-celluloses renders these bodies very easy of attack by oxidising agents, and also to slow oxidation by the oxygen of the atmosphere. The ligno-cellulose complex is more resistant to bacterial action than cellulose.

The ligno-celluloses possess the property of acting upon a photographic plate, in the dark, producing definite pictures.[2] This action takes place slowly at ordinary temperatures, but at 50–55° C. becomes comparatively rapid. On destructive distillation products very similar to those yielded by cellulose are obtained.

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[1] " The Resinic Constituents and Coking Propensities of Coals," *Proc. Roy. Soc.*, 1922, A100, 582–598. See also *Gas World*, Coking Section, April 1st, 1922, pp. 16–20.

[2] W. T. Russell, *Phil. Trans.*, B. 197, 281, 1904, and *Proc. Roy. Soc.*, B., 75, 385, 1906, 80, 376, 1908.

Pecto-celluloses. Some workers consider these substances as forms of soluble ligno-celluloses. They are more readily soluble and much easier to decompose than the other constituents of plant cells. Pecto-cellulose occurs in quantity in unripe fruits.

Cells of plants contain a variety of substances, the chief of which will now receive consideration.

Protoplasm. This is the living material of plant cells, and is more or less fluid in nature. It is in all probability a complex of substances which when dead exhibit the properties of the proteids. It contains the elements carbon, hydrogen, oxygen, nitrogen, and sulphur. In nuclear protoplasm the element phosphorus occurs also.

Aleurone or Protein Grains. These are protein substances which occur in the cells in the form of solid grains, and they constitute the reserve food-material of the plant in connection with nutrition.

Starches (*Polysaccharoses*) $(C_6H_{10}O_5)n$, and *Sugars* (*Monosaccharoses*) $C_6H_{12}O_6$, and (*Disaccharoses*) $C_{12}H_{22}O_{11}$. These substances belong to the carbohydrate group of organic compounds.

Starch is intimately connected with the nutrition processes of plants, and it is found in plant cells in the form of grains, being most abundant in those parts of the plant which serve as store places of reserve material.

The sugars are found in plants dissolved in a watery fluid called cell-sap, and like starch they play a part in plant metabolism. Both starch and the sugars when treated with mineral acids of certain strengths yield substances of a brown colour known collectively as ulmins.

Chlorophyll. The green colour of certain portions of plants is due to this material. It occurs in the chloroplasts of young cells, and it plays a very important part in the metabolism of plants. Chlorophyll is actually a mixture of Chlorophyll-a, $(C_{32}H_{30}ON_4Mg)(COOCH_3)(COOC_{20}H_{39})+\frac{1}{2}H_2O$, and Chlorophyll-b, $(C_{32}H_{28}O_2N_4Mg)(COOCH_3)(COOC_{20}H_{39})$. The presence of the element magnesium in these substances should be noted particularly; it possibly accounts for some of the magnesia found in the ash of fusain, vitrain, and particularly clarain (see page 53).

Two other colouring matters are found in the chloroplasts, one is of a coppery colour, and is called carotin. It is a hydrocarbon of the formula $C_{40}H_{56}$, and is identical with the substance which gives carrots their colour. The other is known as xanthophyll, a substance of a dark brown-red tint of the composition $C_{40}H_{56}O_2$. It appears to be an oxidation product of carotin.

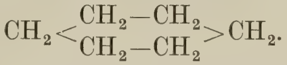
Resins. These substances occur in many cells in various forms, they have no uniformity of constitution, and they present wide differences in chemical character.

For our purpose Colophony may be taken as an example. This substance is present in large quantities in the turpentine obtained from various species of Pinus (pine trees). It consists chiefly of α, β, and γ abietic acids $C_{44}H_{64}O_5$ (Maly); $C_{20}H_{30}O_2$ (Fahrien); $C_{19}H_{28}O_2$ (Stope and Wheeler's monograph); with about

10 per cent. of resenes. It should be noted that Maly's formula is the one now generally accepted. Colophony is a brittle, almost transparent substance, with a vitreous lustre, and it varies in colour from a very pale straw to a dark brown-red. It is interesting to note that the late Dr. W. J. Russell found resinous substances extracted from wood possessed the power to produce pictures when exposed to a photographic plate in the dark, and that para-abietic acid was particularly active in this respect.

When rosin is submitted to destructive distillation, gas, water, and acetic acid, light oil, heavy oil, and pitch are obtained. The gas is composed chiefly of carbonic oxides and olefines, the light oil contains olefines, limit hydrocarbons, terpenes ($C_{10}H_{16}$) and turpinol [$(C_{10}H_{16})_2H_2O$], and the heavy oil, terpenes, naphthenes, and hydrocarbons of the benzene series, *e.g.* toluene, xylene, etc.

Fatty or Fixed Oils. These substances as they occur in plants are mixtures of the glycerol esters of the fatty acids. As an example of a glyceride we may take triolein [$C_3H_5(OC_{18}H_{33}O)_3$].

If triolein is destructively distilled under pressure gases are given off and a distillate obtained which contains: (*a*) limit hydrocarbons (paraffins) $C_nH_{2n}+_2$, type, methane, CH_4; (*b*) hydrocarbons of the ethylene series C_nH_{2n}, type, ethylene, C_2H_4; and (*c*) naphthenes (hydrocarbons of the hydro-aromatic series), C_nH_{2n}, type, cyclo-hexane,  $CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>CH_2$. There is also a pitchy residue which contains waxy bodies probably of the paraffin series.

The destructive distillation of the lime soap of menhaden oil, a fish oil, yielded a distillate which contained hydrocarbons of the ethylene series, and aromatic compounds, such as benzene, toluene, and the xylenes.

Cholesterol $C_{27}H_{45}OH$. This substance occurs in the green cells of plants, and it probably functions in the metabolic processes.[1] It is a solid alcohol, which crystallises from chloroform in the form of needles. On submission to destructive distillation hydrocarbons are formed.

Tannins. These substances occur in the cortical cells of plants, and according to their origin they vary in composition and properties. Usually the tannins are combined with glucose [$CH_2OH\ (CH\ OH)_4CHO$], and upon hydrolysis yield this substance and gallic acid [$C_6H_2(OH)_3COOH$].

Pectin Substances. These substances occur in many fruit juices and also in the stems, roots, and other portions of plants. They are coagulable, and when hydrolysed yield pentoses ($C_5H_{10}O_5$) and hexoses ($C_6H_{12}O_6$), members of the monosaccharose class of the carbohydrates.

Inorganic Salts, such as nitrates, sulphates, and phosphates, occur in the cells of plants.

Bark is a mass of dead tissue, which lies outside the active cork-cambium of the plant. It usually contains tannin compounds, and sometimes resinous substances and esters of the fatty acids.

Cork consists of a number of layers of suberised cells, some of which have thin walls and others thick walls. The former cells generally contain air, and the latter often a reddish brown substance (phlobaphene), which consists mainly of tannins and their derivatives.

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[1] A. Tschirch, *Ber. d. deutsch. Bot. Gesell*, 1904, p. 419.

It will be of interest at this point to consider what is obtained from wood when it is submitted to destructive distillation. The nature of the distillates vary somewhat according to the kind of wood distilled; for instance, in the distillates from resinous woods, terpenes and small quantities of resin occur, these substances being absent from the distillates of other types of wood.

Upon destructive distillation wood yields the following: (*a*) gas, (*b*) acid water, (*c*) wood tar, (*d*) charcoal. The gas consists of a mixture of carbon dioxide, carbon monoxide, methane, ethylene, hydrogen, nitrogen, and a trace of oxygen. The acid water contains chiefly, acetic acid, acetone, and methyl alcohol. Upwards of thirty different compounds have been identified in wood tar, and among these are: trimethylamine, pyrocatechin, benzene, toluene, xylene, cumene, cymene, chrysene, phenol, cresols, xylenols, guaiacol, and higher paraffins.

If the assumption that coal is of vegetable origin is correct then it is reasonable to expect to find in this material evidence in the form of preserved plant remains, and also their degradation products. Although the plant tissues will have undergone profound changes in the process of formation of coal, it is certain from experimental evidence, to be referred to later, that some portions exist in the coal in the unaltered state. It must not be imagined that in the alterations which have taken place all the substances just mentioned (pages 13–16) in connection with the breaking down of cell constituents and contents, have been formed, or that they all exist in coal. Without doubt some of them do, such as carbon dioxide, methane, and certain of the higher solid paraffins, ulmins, etc. A study of them is instructive, however, in connection with their occurrence in the tars resulting from the destructive distillation of coals, and also in regard to the methods of arriving at the constitution of coal.

There are no cases on record in which the original vegetable matter has been found unchanged, and it is hardly likely there ever will be, but in one or two exceptional instances coal of the Palæozoic era has been found in which the original plant material is so little changed that it may be recognised with ease. A well-known case is that of Toula coal (Papier-kohle) from the Tovarkovo mine in Central Russia, described by Renault.[1] This coal occurs as a separate seam in the mine just mentioned, and it appears to consist almost entirely of sheets of bark, finely striated, of a carboniferous tree called Bothrodendron.

In regard to the lignites and brown coals, it is comparatively easy to identify plant remains in these materials. The brown coals are composed chiefly of the remains of mosses and the lignites of plants of the Angiosperm class, and in formation the former resemble dry peat in the hard, compact state, and the latter are very similar to the forest beds of Sweden and Scotland, but in a more advanced state of change.

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[1] "Note sur les cuticules de Tovarkovo," *Bull. Soc. Hist. Nat. Autun.*, Vol. VIII, *Proc. Verb.*, p. 136, 1895.

In the unstratified clay deposits (under-clays) which often occur immediately below coal seams, fossilised rhizophores, and rootlets of several of the Palæozoic Lycopods, portions of fronds of fern-like plants (Alethopteris lonchitica, Neuropteris gigantea), stems and roots of Calamites, and also leaves and spikes of Cordaites are very frequently found.

Some of the seams of coal in the Lower Coal Measures of Lancashire and Yorkshire contain peculiar calcareous concretions called "coal balls." Inside these nodules are found remarkably well-preserved plant remains, and, owing to the ease with which they can be identified and their anatomy studied, they have contributed very largely to the progress made in working out the botany of the Carboniferous period.

Trunks and stems of trees and also bases of trunks with rhizophores attached are frequently found, sometimes in an upright position, in the sandstones and clays of the coal measures. Examples occur in many parts of the world; for instance, in the Scotch and South Lancashire coal-fields, and those of Belgium, France, Germany, and Nova Scotia. In Britain a fine specimen is preserved in the Victoria Park, Glasgow, and another found at Clayton, near Bradford, is in the Manchester Museum. In some of the preserved hollow trunks of Lepidodendra small conical bodies have been found from time to time. These bodies are known as Lepidostrobi, and have been shown by Sir J. W. Hooker to be the fruit of the tree itself.

Plant impressions in the coal itself, say between the bedding planes, are very rarely found; there are a few cases on record both in this country and on the Continent. The author has seen a specimen showing an impression of a piece of Sigillarian bark.

So much for macroscopical evidence of plant remains in coal formations. What does examination under the microscope tell us?

As an introduction to this part of our subject the reader's attention is called to the fact that on making a very cursory examination of any lump of bituminous coal it will, in almost every case, show a banded appearance, the bands or layers being alternately bright and dull. Now Stopes,[1] after careful examination, distinguishes, not merely bright and dull bands, but four distinctive portions or bands which together form the mass of an ordinary bituminous coal. These different bands can be seen by the naked eye and also microscopically in thin sections of coal, and with care and patience they can be separated by hand. They exhibit various differences in character, and under the microscope markedly distinct features are seen. Provisionally, Stopes named these four bands as under:—

(*a*) Fusain. The equivalent of "mother-of-coal," "mineral charcoal," etc., of various authors.
(*b*) Durain. The equivalent of "dull" hard coal of various authors; the "Mattkohle" of the Germans.
(*c*) Clarain. } Together the equivalent of "bright" or "glance" coal of various
(*d*) Vitrain. } authors; the "Glanzekohle" of the Germans.

It is a very difficult operation to prepare a thin section of coal, so that it can be examined under the microscope by transmitted light. The process is a tedious one, and requires special technique. Among those who have made a special study of this method of examining coal are Lomax, Jeffrey, and Thiessen. The history of the development of the microscopic study of coal is dealt with in an excellent manner by White and Thiessen in a memoir[1] which contains many microphotographic illustrations. Jeffrey[2] and Lomax have[3] also contributed to the literature dealing with the microscopic examination of coal. J. J. Stevenson,[4] between the years 1911 and 1913, published several important works dealing with the formation, structure, etc., of coal, and he states: "One quickly discovers that intimate structure of coal can be ascertained only by aid of the microscope, since to the unaided eye the great mass of coal is wholly structureless."

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[1] *Proc. Roy. Soc.*, 1919 (B.), 90, 470.

It appears that the microscopic investigation of coal first received attention in the year 1833 by H. Witham, this worker undoubtedly being the pioneer in microscopic work on coal. When one bears in mind the difficulties at that time in regard to obtaining satisfactory instruments, it is remarkable what good work was done by this worker. From sections which he made of Bovey coal he, so he states, observed "an indistinct resemblance to coniferous structure" made evident by the appearance "in parallel series of square or hexagonal marks."

Later in 1838 Frederick Link was able to confirm the discoveries made by Witham and also those of Hutton (1834). It appears that in order to render his coal fragments more transparent for microscopic study he boiled them in kerosene or rectified petroleum, and he made accurate drawings of what he observed under the microscope. Link applied his results to a theory for the origin of coal, and came to the conclusion that coal originated from peat on account of the presence of plant remains in it.

Following Link, Petzholdt (1841) carried out some work on mineral charcoal, now know as fusain, and from his observations came to the conclusion that this material and therefore coal was made of the remains of decomposed plants.

In the year 1842 Phillips ashed a Staffordshire coal, and on making a microscopical examination of this ash he found vegetable or plant tissue skeletons.

Among much other work on coal, Dawson, who published his first work on this substance in 1846, carried out a considerable amount of investigation on the so-called "mother-of-coal" (fusain), and in 1883 identified in this material the recognisable remains of wood cells belonging to many plant genera which contributed towards the formation of coal. Among these may be mentioned the Sigillaria, Lepidodendron, and the Cordaites. This worker in a large number of cases treated the fragments of fusain by chemical means before examining under the microscope. This method of preparing coal for the microscope was used by Schulze, who, in 1855, published a paper in which he described his method. The solution he used, known under the name of Schulze's solution, is a mixture of nitric acid and potassium chlorate. One method of making this solution is to take nitric acid of a specific gravity of 1·2 and add to it about 2 per cent. of potassium chlorate. If this mixture is used cold then the coal fragments must be left in it for several hours before they are ready, but if it is gently warmed until gas is freely given off then five minutes to a quarter of an hour is sufficient time for immersion. The fragments are then removed from the solution, washed first with water and then with ammonium hydroxide, and finally with hot alcohol, after which they can be mounted for examination.

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[1] "The Origin of Coal," *U.S. Bur. of Mines. Bull.*, 38, p. 227, 1913.

[2] "Methods of studying Coal," *Conspectus*, Vol. VI, No. 3, 1916.

[3] "The Microscopical Examination of Coal," *Trans. Inst. Mining Eng.*, Vol. 42, Part 1, pp. 1–20. See also *Trans. Inst. Mining Eng.*, Vol. 46, Part IV, pp. 592–635.

[4] "Formation of Coal Beds," *Proc. Amer. Phil. Soc.*, Vol. 50, 1911, pp. 1–116, 519–643; Vol. 51, 1912, pp. 423–553; Vol. 52, 1913, pp. 31–162. Also book, publ. New Era Co., Lancaster, U.S.A., 1911–1913.

In the year 1870 Huxley, in an article entitled "On the Formation of Coal,"[1] indicated that the coal of the "Better Bed," occurring in Bradford district, Yorkshire, was composed chiefly of sporangia and spores. Later, in 1874, Williamson[2] pointed out that what Huxley called sporangia were actually megaspores. Since this period a considerable number of varieties of megaspores (and also microspores) have been found in British coals and those from other countries.

Among other workers on the microscopic investigation of coal may be mentioned Tieghem (1879), Renault (1881–1900), Fischer and Rüst (1883), Bertrand (1892), Potoniè (1904–10), and Barsch (1908).

In 1908 Stopes and Watson[3] investigated the microscopic structure and origin of concretions of mineralised plant debris found in the mass of certain coals and known in general terms as "coal balls" (see Fig. 4). There seems little doubt that these petrified masses were formed in the debris from which coal emanated after its accumulation, and were not transported at some later date to the spots at which they are now found.

"Coal balls" from almost every deposit in which they occur contain remarkably well-preserved plant remains, and in such a small section as 5 inches by 3·5 inches cut from one of these concretions there may be fifteen or more fragments of lepidodendron, calamites, myeloxylon, and fern petioles. In these nodules rhizophores and roots of the plants just mentioned and of other carboniferous plants are often found in abundance. Much of the plant remains is in a partly decomposed condition, and generally a large quantity of a brown substance, devoid of structure, is found. The presence of this material is especially in evidence in those cases in which most of the softer portions of the plant remains have disappeared, and only the more resistant portions (xylem, cork, etc.) have been left.

In addition to plant remains, "coal balls" are composed of mineral matter, such as calcium, magnesium, and iron carbonates with small amounts of calcium phosphate and with varying quantities of clay, shale, or sand. Analyses, by Stopes and Watson, of some of these nodules showed calcium carbonate varying between 49·35 and 91·09 per cent. and magnesium carbonate up to as high as 42·82 per cent.

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[1] *Contemporary Review*, Vol. 15, pp. 618–629, 1870.

[2] "On Coal and Coal Plants," *MacMillan's Mag.*, Vol. 29, pp. 404–417. London, 1874.

[3] "On the Present Distribution and Origin of the Calcareous Concretions in Coal Seams, known as 'Coal Balls,'" *Phil. Trans. Roy. Soc.*, Lond. Ser. B., Vol. 200, pp. 167–218.

Iron pyrites was also found by these workers in amounts up to 3·27 per cent. They vary very much in size from minute nodules to bodies a number of feet in diameter. A very large "coal ball" weighing about two tons was found in a mine at Shore; so large, in fact, was this concretion that it almost completely cut out a coal seam.

It is very probable that "coal balls" were formed at a very early stage in the history of the coal seams in which they are found. As stated by Moore,[1] "in addition to the preservation of the plant structures . . . the vegetal matter has been squeezed down around the balls while they have been scarcely compressed. They must have been in existence before the compression of the vegetal matter occurred, and the presence of slickensides shows that the coal and accompanying rocks were squeezed around them. It is only reasonable to suppose that these concretions were formed on the bottom of the marsh in which the vegetal matter grew, and that they may have originated by the action of algæ or other low forms of plants causing precipitation of calcium carbonate, as many calcareous concretions originate at the present day. As they grew, fragments of plants came in contact with them and were enclosed."

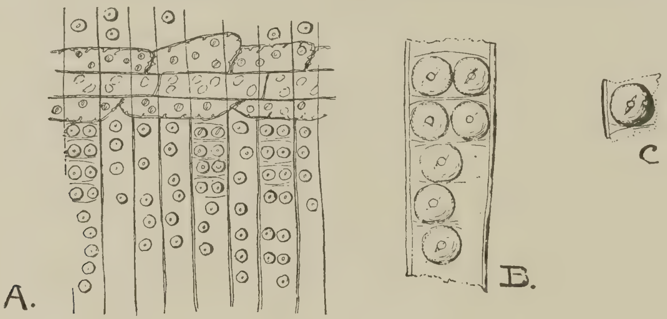

FIG. 1.

A. Small portion of longitudinal section of coniferous wood.
B. Single tracheid from the same, enlarged.
C. Small fragment from the same, showing characteristic feature.

(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

In 1910, Jeffrey published a new and satisfactory method of his own discovery,[2] which enabled him to cut pieces of coal into thin sections with a microtome. This process did away with the necessity of grinding down in order to form thin sections, and seemed to have in its favour the fact that a large number of sections could be cut from the same piece of coal. It necessitated, of course, the softening of the piece of coal on the one hand, and the removal of the mineral matter contained therein on the other. For particulars of the methods used the reader is referred to the original paper. Jeffrey's microscopical investigations proved without doubt that coal is formed from plant remains.

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[1] *Coal, its Properties, Analysis, Classification, Geology, Extraction, Uses and Distribution.* London, Chapman & Hall, Ltd., 1922.

[2] "The Nature of some supposed Algal Coals," *Proc. Am. Acad. of Arts and Sci.*, Vol. 46, pp. 273–290. 1910.

A series of interesting papers illustrated with a number of microphotographs, showing that coal contains well-preserved and numerous plant tissues, were published by Lomax between the years 1911 and 1915.

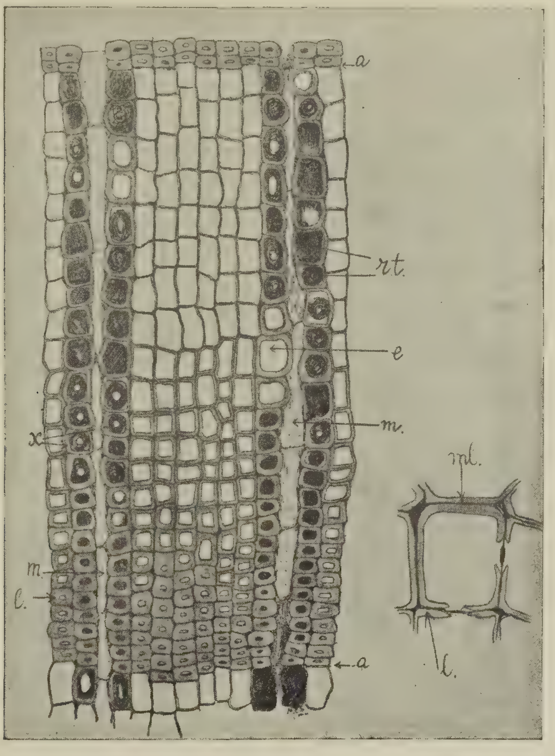

Fig. 2.—Transverse Section of a small portion of a Simple Wood.

Showing the intimate association of different types of substances composing it. The squarish cells are "wood elements" (tracheids) with lignocellulosic walls, much thicker in the region of the autumn wood *a* than in the elements formed earlier in the year. A single tracheid on the right is enlarged to show the relation of the "middle lamella" (*ml*) to the lignocellulosic wall *l*. In the diagram, *rt* are tracheids filled with resin spools. The medullary rays (*m*) contain protein substances, and also may contain resin. (Magnified about 100 diameters.)

(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

In the year 1913, White and Thiessen published an exceedingly valuable memoir on coal, and a large section of this work is devoted to the microscopical side of the question. Thiessen deals with this section, and illustrates his text by a large number of microphotographs, all of which prove decisively that coal is of vegetable origin. This worker improved upon Jeffrey's method of section cutting with a microtome, but in the preparation of his coals for microscopical examination he used the modified Jeffrey method, and also a method of grinding down to form thin sections. He dealt microscopically with the following coals: lignites, sub-bituminous, cannel, and bituminous coals. His chief conclusions were that in the case of lignites, these consisted of the most complex debris of all coals; that in regard to cannel coals the "algæ," which Bertrand and Renault considered they were composed of, did not exist, and that these coals are composed mainly of spores; that the older bituminous coals are more complex in substance than the cannels, and to an extent comparable with the lignites though "there is a gradual loss of wood as one goes from the lower to the higher grades." He further concludes that "all coal was laid down in beds analogous to the peat beds of to-day," and that "coal . . . is chiefly composed of residue consisting of the most resistant components of plants, of which resins, resin waxes, waxes, and higher fats, or the derivatives of the compounds composing these, are the most important."

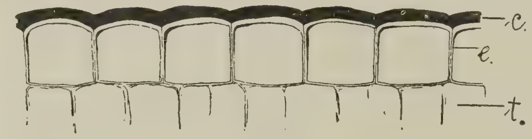

FIG. 3.—DIAGRAM OF VERTICAL SECTION OF EPIDERMIS CELLS.

(*e*) Showing the Cuticle layer.
(*c*) Common to them all.
(*t*) Inner tissue of the leaf.

(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

Among the microphotographs prepared from coal by Thiessen are to be found one showing megaspores on which the air sacs and tri-radiate lines can be seen, another in which practically undamaged spores are visible (from a Pittsburg coal), another showing flattened spores with xyloid tissue, and another, prepared from a bituminous coal, showing numerous particles of resin. Jeffrey during his investigations made sections of cannel coal, and produced a microphotograph from a section of this coal which showed that it consisted practically of flattened spores.

Attempts have been made to obtain photographs of the surfaces of various coals, using oblique or vertical illuminations, and Winter[1] published some microphotographs prepared by this means, showing indications of cellular structure.

White[2] pointed out the presence of resins in coal, and showed microscopically

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[1] H. Winter, "Die mikroskopische Untersuchung der Kohle im auffallenden Licht." *Glückauf*, Vol. 49, pp. 1406–1413. Pl. V. Essen, 1913.

[2] "Resins in Palæozoic Plants and in Coals of high rank." Professional paper 85, Part E, *U.S. Geol. Survey*, pp. 66–83, Pls. 9–14. Washington, 1914.

"thread-like rods of what appeared to be resins in such positions that the conclusion seems demonstrated that they represent the fillings of the 'gun canals,' so often anatomically described from microscopic sections of the genera of coal measure plants known as petrifactions."

Stopes and Wheeler have carried out a very considerable amount of microscopic investigations on coal, and much of this very valuable work is recorded in their monograph on the Constitution of Coal.[1] This work is illustrated by two diagrams and seventeen very excellent microphotographs, and some of these are reproduced in Figs. 1–10. These workers point out the great difficulty surrounding the identification of plant remains in coal sections, and state "to one unaccustomed to fossil plants, and inexperienced with the microscope, a 'recognisable' plant fragment must be startlingly perfect and conspicuous, or it would not stand out from the confused debris and catch the eye." They have accomplished the separation of the individual wood vessels from lignite artificially by the use of chemical solvents and watched under the microscope "lignified walls, with their characteristic pitting, fall apart and lie separately, each from each, as the middle lamellæ dissolved." From this experiment they conclude that it shows some indication of "what must have happened many times during the processes of coal formation, and may account for the number of more or less isolated clear-walled (not carbonised) wood elements to be found scattered in coal."

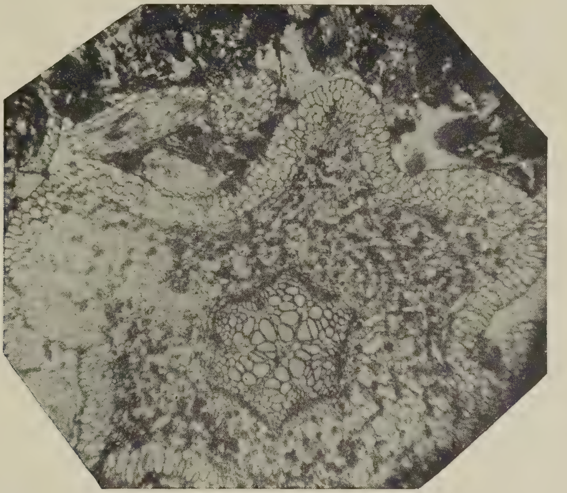

Fig. 4.—Transverse Section of a "Coal Ball."
Containing Pteridosperm rootlet tissues nearly perfectly petrified.
(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

"Mother-of-coal," "carbonised wood," or fusain, as it is now called, is the dull charcoal-like substance which is found in practically all coal, particularly on the bedding planes. It contains plant tissues, but in a more or less disintegrated state. As already mentioned on page 18, Dawson was able to recognise plant remains in this material.

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[1] "Monograph on the Constitution of Coal." H.M. Stationery Office, 1918.

In the opinion of Stopes and Wheeler, cork is an important constituent of coals, and they have found very frequently in "coal balls" well-preserved cork layers. Hickling,[1] in a paper read before the Manchester Geological and Mining Society, stated that in his microscopical observations on coal the great majority of preserved structures he observed were cortical tissues.

Cuticles of plants in the preserved state occur very frequently, and Stopes and Wheeler state "in nearly all coals, such sheets or smaller fragments of them (of cuticle), are very common and generally lie horizontal with the bedding plane of the coal." White and Thiessen, Lomax, Grand'Eury, and others confirm the presence of cuticles in coal.

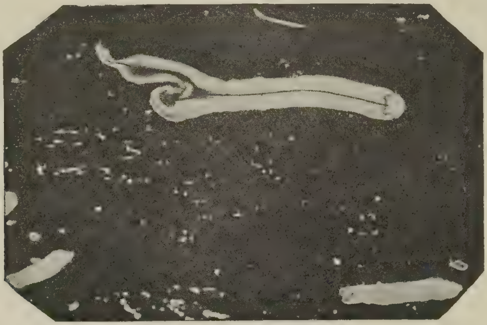

Fig. 5.—Section of a Macrospore from English Bituminous Coal.

The thin black line in the spore represents the collapsed, once nearly spherical space of the spore. (Magnification 30 diameters.)

(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

Spores, spore coats, seeds, soft-walled tissues, and other portions of plants have been found in coal upon microscopic examination, chiefly by the workers who have already been mentioned in this section of the chapter.

Comparing vitrain, which is very bright in its appearance, and clarain, the lustre of which is somewhat subdued, with durain, Tidswell and Wheeler[2] state "from chemical examination alone, one might be tempted to say that durain is durain because it is rich in ash; but it is clear from the work of Stopes that the decisive factor affecting the lustre is the presence or absence of plant structure.[3] No doubt there is a direct connection between the ash content of a coal and the presence of plant remains therein."

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[1] "Micro-petrology of Coal," *Coll. Guard.*, Vol. 113, pp. 941–943. London, 1917.

[2] J.C.S. *Trans.*, 1919, 115, 631.

[3] See also D. B. Dowling, "The Formation of Coal," *Proc. Trans. Roy. Soc., Canada*, Vol. 4, pp. 23–35. 1910.

This does not mean that vitrain and also clarain are not the products of the decomposed vegetable matter, for even plant remains have been detected microscopically in these two constituents of banded coal, but in small quantities only. Stopes and Wheeler[1] state " . . . in our own experience the 'bright' bands show the better preserved tissue, which, however, may be masked by a uniformity of colour in the section."

Seyler[2] also points out that "bright" coal on microscopic examination shows the remains of woody tissue. In this connection it is interesting to note that by heating clarain with concentrated nitric acid containing a little hydrofluoric acid, A. Baranov and W. Francis[3] obtained a moderately light brown solution and residue of transparent fragments. This residue amounted to between 5 to 10 per cent. by weight of the coal treated and consisted chiefly of fragments of cuticles with a few broken spore exines.

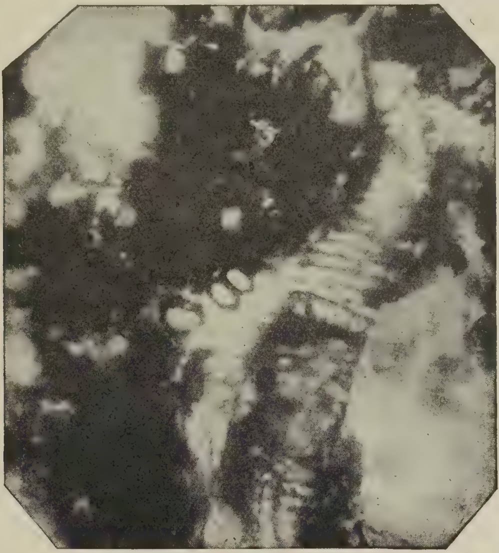

FIG. 6.

Very much enlarged, single tracheids from the apparently unorganised mixed debris forming a considerable part of ordinary bituminous coal. (Magnification 300 diameters.)

(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

Although not actually concerned with the microscopic investigation into the constitution of coal, but rather with its formation, it is interesting to note that several species of bacteria have been identified in coal sections. To the biologist it is well known that in the first processes of decay microörganisms play an important part, and it is quite certain that when plants of the coal age died and fell they were attacked by those species of microörganisms which assist in the disintegration of plant tissues, and their activities continued until the decaying material became too acid for their existence. Different species of microörganisms have the power of decomposing protein bodies, fats, sugars, starches, ligno-cellulose, and cellulose. Plant tissues consist in the greater part of the last two materials, and the destruction of these substances may be accomplished (*a*) by aerobic organisms, (*b*) by anaerobic organisms, (*c*) by denitrifying bacteria, and (*d*) by molds. During the bacterial disintegration of cellulose, methane, carbon dioxide, hydrogen, and other gases are set free (Popov, Tappeiner, and Hoppe-Seyler), and this fact is worthy of note.

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[1] *Monograph on the Constitution of Coal.* H.M. Stationery Office, 1918.

[2] Boulton's, *Practical Coal Mining*, Vol. 1, p. 67. London, 1907.

[3] "Banded Bituminous Coal," *Fuel*, 1922, 1, 219–222.

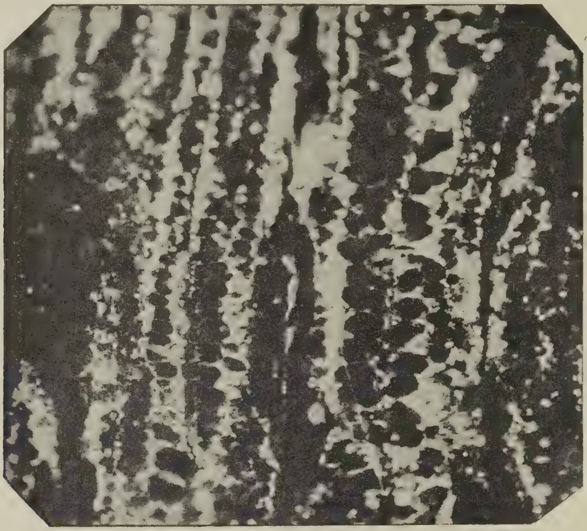

Fig. 7.

Tangential section through the mesophyll (soft tissues) of leaves in ordinary bituminous coal. (Magnification 100 diameters.)

(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

Renault, who spent a considerable amount of his time in studying the occurrence of microörganisms in coal, published several works on this subject, and illustrated these with plates and figures.[1] In addition to other microörganisms this worker

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[1] "Recherches sur les Bactériacées fossiles," *Ann. Sci. Nat. Sér.* 8 *Bot.*, Vol. 2, pp. 275–349. Text figs. 1–46. Paris, 1896.

"Les microorganismes des lignites," *Comp. Rend. Acad. Sci.*, Vol. 126, pp. 1828–1831. Paris, 1898.

Renault, B., and Roche, A., "Notice sur la Constitution des Lignites et les recognised representatives of living forms of bacteria of the family Coccacæ, such as Micrococcus and Streptococcus. Excellent examples of micrococci were found in the cuticle of the bark of the carboniferous tree, Bothrodendron, of which the Papier-Kohle (paper coal) or Toula coal of Russia is composed entirely.

The examination of coal sections for bacteria is not an easy matter, and it requires much experience and biological knowledge. There are many objects which may be mistaken for bacteria, such as specks of mineral matter, badly formed crystals of organic matter, foreign matter introduced during the preparation of the sections, etc., and some authorities, including Dr. E. S. Moore, of Pennsylvania, who had the privilege of examining Renault's original slides, are convinced that even this worker

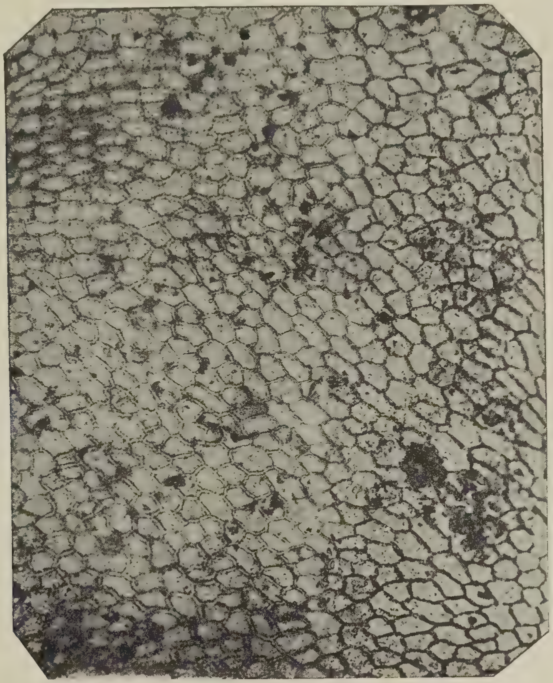

Fig. 8.—Sheet of Cuticle from Russian Coal.
Showing the impress of the cell structure upon it.
(Cf. Fig. 3.) (Magnification 130 diameters.)
(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

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organismes qu'ils renferment," *Bull. Soc. Hist. Nat. Autun.*, Vol. 2, reprint, pp. 1–39. Pls. XI–XIII. Autun, 1898.

"Sur quelques microorganismes des combustibles fossiles," *Bull. Soc. l'Indust. Minér.*, Vol. 13, Livr. 4 (1899) and Vol. 14, Livr. 1 (1900), pp. 460, 66 Text figs. 8vo. and atlas. 30 folio plates. St. Etienne, 1900.

"Du rôle de quelques bactériacées fossiles au point de vue géologique," *Congrès Géologique International*, pp. 646–663. 1900.

has at times mistaken other material for bacteria. However, a great many of his slides do show preserved bacteria, and evidence that these organisms have played their part in the breaking down of the tissues of plants which have ultimately formed coal is practically conclusive.

Without doubt the occlusion of gases in coal is very intimately connected with its constitution, especially as some of them are degradation products of plant constituents. The chief gases found in coal mines, which are given off by the coal at practically ordinary temperatures and pressures, are methane (CH_4) and carbon dioxide (CO_2); very small quantities of carbon monoxide (CO) are found in some mines. Methane, as a general rule, comes away from the coal silently and at a more or less regular rate, but at times large quantities are discharged from faults or from fissures (breakers) in the roof and floor of excavations. Occasionally sudden outbursts from the coal take place, the methane coming away with a noise resembling a boiler blowing off steam. These outbursts are called blowers, and the gas in some cases continues to come away for a number of years. Carbon dioxide is given off by the coal silently, and occurs in greater quantities in shallow damp mines than in dry deep ones. According to Thomas the amounts of methane and carbon dioxide in the gases from almost all blowers and from borings in seams is over 90 per cent. and less than 1 per cent. respectively.

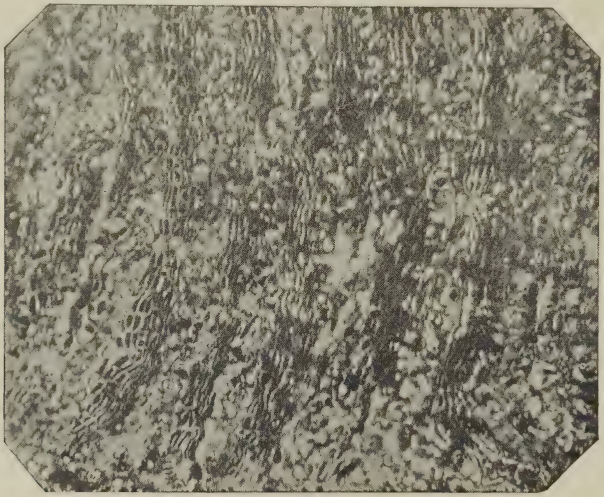

Fig. 9.

Masses of cork tissue in coal from Dillenburg. (Magnified 50 diameters.)

(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

The amount of gas (chiefly methane and carbon dioxide) which is given off in some mines is very large, amounting to many thousands of cubic feet, and a gaseous mine in the anthracite region of Pennsylvania has emitted as much as 2400 cubic feet of methane per minute.

Chamberlain[1] has shown that when coal is pulverised it gives off a large quantity of methane and a little ethane ; but if the same coal is allowed to remain in a closed vessel for several months at the ordinary temperature and in a vacuum, considerably larger quantities of the same gases are given off.

It should be noted that the amount of both methane and carbon dioxide which comes away from coal after removal from the mine varies greatly with different coals, but in almost all cases the quantity which escapes during the first day or so is much larger than that given off with an increase in the period of time of exposure.

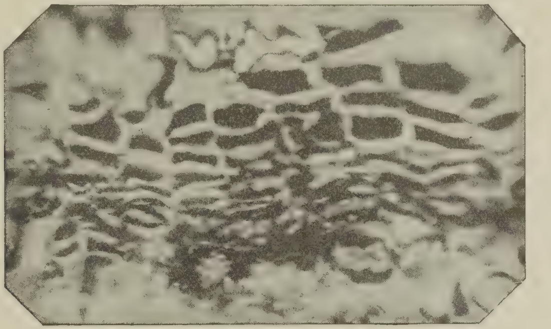

Fig. 10.

Part of Fig. 9 more enlarged to show the zone of the cork cambium. (Magnification 250 diameters.)

(*Courtesy Dr. M. C. Stopes and H.M. Stationery Office.*)

A fact which must not be lost sight of is that, in addition to methane and carbon dioxide, oxygen, nitrogen, carbon monoxide, and sometimes sulphuretted hydrogen escape from coal when it is kept *in vacuo* at ordinary temperatures.

Some doubt has been thrown upon the contention that the gases in coal exist as occluded gases,[2] and Munro,[3] from the results of some careful experiments, formulates the hypothesis that "gases are present in a state of solid solution in coal, the solubility of carbon dioxide being high, whilst the solubility of oxygen and nitrogen is low."

If various kinds of coal are heated at 100° C. in a vacuum the following gases are obtained : methane, carbon dioxide, nitrogen, oxygen, carbon monoxide, and in a few cases sulphuretted hydrogen.

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[1] "Notes on Explosive Mine Gases and Dusts," *U.S. Geol. Survey, Bull.*, 383. 1909.

[2] H. C. Porter and F. K. Ovitz, "The Escape of Gas from Coal," *U.S. Bur. of Mines*, Tech. Paper 2. 1911.

[3] A. D. Munro, "The Occlusion of Gases in Coal," *J.S.C.I.*, April 29th, 1922, pp. 129T–132T.

From Scotch and English cannel coals Thomas[1] obtained gases the compositions of which varied as below :—

CO_2	6·44 to 84·55 per cent.	
CH_4	77·19 to 80·69 per cent.	Absent in three samples.
C_2H_6	2·67 to 7·80 per cent.	Absent in two samples.
C_3H_8	0·91 per cent.	Present in one sample only.
N_2	5·96 to 40·06 per cent.	

Another table by the same worker[2] gives the average figures for three classes of coal :—

	CO_2 per cent.	N_2 per cent.	CH_4 per cent.	O_2 per cent.	CO per cent.
Anthracite .	8·7	2·6	88·7	—	—
Steam . .	9·8	9·1	80·5	0·5	—
Bituminous .	18·0	19·8	59·6	2·6	—

Munro[3] worked upon the lignites, pitch coals, and brown coals of New Zealand, and some of the results obtained by him are given below :—

Coal.	CO_2 per cent.	N_2 per cent.	CH_4 per cent.	O_2 per cent.	CO per cent.	H_2S per cent.
Avoca (brown coal) .	80·5	19·5	—	—	—	—
Mossbank (pitch coal) .	90·7	8·7	—	0·6	—	—
Coal Creek (brown coal) .	97·7	1·9	—	0·2	—	—
Puponga (pitch coal) .	80·4	19·6	—	—	—	—
Blackball 1 (brown coal) .	23·2	35·9	31·8	—	—	9·1
Ditto 2 ditto . .	62·6	7·7	28·6	—	1·1	—
Pt. Elizabeth 1 (bitumen)	46·4	9·2	43·3	—	0·6	—

The nitrogen present in the gases which escape from coal is in all probability due mainly to air which has become imprisoned during the formation of the coal, and not to any great extent to the degradation of the nitrogen constituents of the vegetable matter from which coal has been formed ; the oxygen of the same air being for the most part used up in the processes of decay.

Much useful information on the subject of gases in coal will be found in the papers of E. von Meyer,[4] Zitowitsch,[5] Thomas,[6] McConnell,[7] Bedson,[8] Trobridge,[9] Barker,[10] Porter,[11] and Munro.[12]

With the object of throwing some light upon the constitution of coal, a considerable amount of research has been carried out on the action of solvents on this substance. Work in this connection has been very carefully done with the idea in mind of extracting the constituents of the coal in an unchanged condition, but unfortunately up to the present it is very doubtful whether the attempts which have been made have been rewarded with much success. Several types of solvent have been employed in these investigations; among them may be mentioned pentane, petroleum ether, chloroform, acetone, ether, ethyl alcohol, amyl alcohol, acetic anhydride, glacial acetic acid, carbon disulphide, benzene, phenol, pyridine, and various mixtures of these solvents.

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[1] *J. Chem. Soc.*, 1876, 39, 144.

[2] *J. Chem. Soc.*, 1875, 28, 793.

[3] *J. Soc. Chem. Ind.*, 1922, 41, 129T–132T.

[4] *J. prakt. Chem.*, 1872, 5, 144 ; 1872, 6, 389.

[5] *J. prakt. Chem.*, 1872, 6, 79.

[6] *J. Chem. Soc.*, 1875, 28, 793 ; 1877, 32, 146.

[7] *J. Soc. Chem. Ind.*, 1894, 25.

[8] *Trans. Fed. Soc. Min. Eng.*, 1902.

[9] *J. Soc. Chem. Ind.*, 1906, 1129.

[10] *Trans. Amer. Inst. Min. Eng.*, 40, 24–31.

[11] *U.S. Bur. Mines, Bull.*, 82, 50.

[12] *J. Soc. Chem. Ind.*, 1922, 41, 129T–132T.

It will, no doubt, occur to the thoughtful reader that in order to remove unchanged any substance from the coal, the solvent used should not exert any chemical action upon the substance itself or upon the residue. When the solvents named above are carefully considered, it will be seen that some of them are not above suspicion in regard to this matter; for instance, acetic anhydride, acetic acid, phenol, and pyridine, so the choice might fall upon petroleum ether, ether, acetone, or benzene as very suitable solvents; but in cases in which they have been used the results have turned out somewhat disappointing, as only very small quantities of substance are extracted.

In the use of benzene somewhat better results have been obtained. Watson Smith[1] submitted several coals to the action of pure benzene, and obtained amounts of extractive as follows:—

From an Australian cannel coal . . .	0·67 per cent.
,, American cannel coal . . .	1·06 ,,
From a Japanese bituminous coal . .	9·5 ,,

The Japanese coal was of a bituminous nature, and was obtained from the Miike mine. This coal, according to the view of Donath, belongs to the Tertiary Age. The benzene full extract from it was semi-fluid, somewhat like tar, but possessed a smell resembling crude petroleum. Watson Smith submitted the extract to distillation and obtained the following fractions:—

175–200° C. . . .	Light naphtha.
250–300° C. . . .	Toluene (or xylene) containing phenols.
Above 300° C. . . .	Solid paraffins.

Pyridine bases were also found in the distillates from the benzene extract. This worker considered that this extract consisted of "bituminised resins" resulting from the degradation of spores, fruits, etc., of a rich vegetation.

It is interesting to note that Dr. Marie Stopes visited the Miike mine and was able to observe *in situ* plant structures, and she came to the conclusion that there is hardly any doubt "that the coal was formed of a mixed forest debris consisting largely of conifers and dicotyledons, and not considerably of 'spores' or 'moss,' as was first suggested in the discussion on Watson Smith's first paper" (1891).

Watson Smith, in co-operation with J. C. Chorley, made two other contributions on the subject: one[2] on the soluble and resinous constituents of coal, and the other[3] on the petroleum-like bitumen of a Japanese coal.

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[1] *J.S.C.I.*, 1891, 10, 975–980.

[2] *J.S.C.I.*, 1892, 11, 591–592.

[3] *J.S.C.I.*, 1893, 12, 221–222.

Some important work was carried out by Pictet and Ramseyer[1] on a Montrambert-Loire coal, using benzene as the solvent. The phenols and bases were removed from this extract by the use of caustic soda and sulphuric acid, after which the solvent (benzene) was distilled off. The residue consisted of a mobile oil which, when subjected to distillation under 10 m.m. pressure, yielded 60 per cent. of distillate between 110° and 265° C. The residue on cooling had the appearance of dull resin; the distillate was redistilled and eight fractions were collected, and all these fractions when exposed to the air suffered oxidation. They were able to isolate, from one of the fractions, a hexahydrofluorene, $C_{13}H_{16}$.

A very important investigation was carried out on a large scale in 1916 by Pictet, Ramseyer, and Kaiser.[2] These workers used 5½ tons of Saare coal in their investigation, and they employed as the solvent boiling benzene, the operation taking four days. The extract was reduced to about 20 litres by distilling off the benzene, and to this residue was added 100 litres of petroleum ether. This precipitated 2·7 kilos of a powder of a light brown colour, and this was not examined further at the time. The liquid, after the removal of the precipitate, was distilled to remove the petroleum ether, etc., and the process was carried on until there was obtained a thick brownish oil, which weighed 10·6 kilos. On examination it was found that this oil contained about 0·5 per cent. of bases and 2 per cent. of oxygenated compounds, the residue consisting of hydrocarbons, both saturated and unsaturated, the former comprising about 25 per cent. of the original material. Several pure hydrocarbons were isolated, namely, C_7H_{10}, C_8H_{12}, and $C_{30}H_{60}$ (melene).

A Westphalian gas coal was extracted with chloroform by Siepmann,[3] and he obtained a dark brown solution possessing a green fluorescence. The amount of solvent-free extract was small, being only 1·25 per cent. of the coal, and it was hard, dark brown in colour, possessing an odour somewhat similar to heavy petroleum. Between 75° and 80° C. it began to melt, and at 100° C. was quite fluid. Decomposition commenced between 130° and 140° C. This worker also extracted another sample of the same coal with ether and obtained a soft yellowish brown, resinous substance possessing an aromatic odour. In this case the amount of extract was very small, being only 0·3 per cent. of the weight of the original coal. The residue of this coal after the ether extraction was further extracted with alcohol, and a dark brown resinous substance was obtained, also possessing an aromatic odour, and amounting to 0·25 per cent. of the original coal. A final extraction with chloroform yielded 0·75 per cent. of a dark brown substance with an odour somewhat resembling coal tar.

Phenol at a temperature of 110° C. was used by Gigunet[4] as a solvent upon a bituminous coal which was reduced to a very fine powder. He found that he obtained as much as 4 per cent. of dry extract. The solution in phenol, on cooling, deposited brown flakes, and if alcohol was added to this solution it precipitated the whole of the dissolved matter in the same form. This worker did not proceed much further in the matter.

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[1] "Ueber einen Bestandteil der Steinkohle," *Ber*, Vol. 44, 2486–2497. 1911.

[2] "Sur quelques hydrocarbures contenus dans la houille," *Compt. Rend. Acad. Sci.*, Vol. 163, pp. 358–361. 1916.

[3] "Beiträge zur Kenntniss der 'harzartigen' (löslichen) Bestandtheile der Steinkohlen," *Zeits. Berg. Hut. und Salinenwesen*, Vol. 39, pp. 26–31. 1891.

[4] "Sur la constitution de la houille," *Compt. Rend. Acad. Sci.*, Vol. 88, pp. 590–592. 1879.

In 1915 Parr and Hadley[1] used phenol as a solvent, and stated that both the extract and the residue absorbed oxygen readily from the air at ordinary temperatures.

It was Bedson[2] in the year 1899 who made the interesting discovery that pyridine, when used as a solvent on coal, extracted large quantities of material, the extract being of a brownish red colour, possessing a green fluorescence. This worker continued his researches,[3] and on extracting with pyridine the bright coal and also fusain separated from the coal dug from the Busly seam (County Durham), obtained from the former about 19 per cent. of extract, and from the latter less than 1 per cent.

Baker, following Bedson in 1901,[4] examined an anthracite coal and also two bituminous coals, one from the Hutton seam, and the other from the Brockwell seam, using commercial pyridine as the solvent. He discovered that anthracite gave very little extract; but quite a considerable quantity was obtained from the bituminous coals, that from the Hutton seam yielding 20·4 per cent. and that from the Brockwell seam 11·5 per cent. of extract. This worker pointed out that the former coal after extraction had lost all its coking properties, whilst the latter retained this property to a slight extent.

It was shown by Anderson and Henderson[5] that the amounts of "volatile matter" present in the residues obtained when they extracted their coals with pyridine, were actually more than found in the original coals. This led Lewes to conclude that the pyridine must have attached itself to some constituent in the coal to form a compound insoluble in excess of pyridine. It is quite possible that Lewes' conclusion is not the correct one, but that some of the pyridine had become absorbed by the coal residue.

A considerable amount of very useful work has been done by treating the pyridine-free extract with other solvents, the object being to obtain compounds of definite composition.

Clark and Wheeler[6] came to the conclusion that pyridine makes a partial separation of coal into two groups of bodies, namely, "humous" and "resinous" respectively. They extracted a pyridine extract which, according to their view, consisted of resinous bodies, with chloroform, and found that between 30 and 40 per cent. of it was soluble in this solvent, yielding a solution of an orange-red colour and possessing a fluorescence. The solid extract was of a colour resembling sepia, it softened at 90° C. and portions of it melted at 102° C. They found that if the pyridine extract was treated with benzene very similar results were obtained.

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[1] "The Analysis of Coal with Phenol as Solvent," *Ill. Univ. Eng. Exp. St. Bull.*, No. 76. Urbana, 1915.

[2] *Trans. Fed. Inst. Min. Eng.*, Vol. 16, pp. 388–390. Newcastle, 1899.

[3] "Notes on the Proximate Constituents of Coal," *J.S.C.I.*, Vol. 27, pp. 147–149. London, 1908.

[4] "The Solvent Action of Pyridine on Certain Coals," *Trans. Fed. Inst. Min. Eng.*, Vol. 20, pp. 159–162. Newcastle, 1901.

[5] *J.S.C.I.*, Vol. 21, pp. 237–242. 1902.

[6] *J.C.S.*, 1913, 103, 1704.

By extracting the chloroform soluble portion of a pyridine extract, obtained from a bituminous coal, with pentane, Jones and Wheeler[1] obtained a solid paraffin which melted between 53° and 59° C. This wax consisted chiefly of heptacosane ($C_{27}H_{56}$).

Bone and Sarjant[2] have shown that the presence of oxygen has a retarding action on the solvent power of pyridine on coal, which varies with the nature of the coal, and which is due to the coal substances becoming oxidised before or during the extraction process. It was pointed out that oxidised coal was much less susceptible to the action of pyridine than coal which had not been submitted to the process of oxidation, and that water also exerted a retarding influence on the extractive property of pyridine. In order to obtain concordant results, it is necessary to use dry coal ground to a standard size, to exclude air, to extract with a purified and dried pyridine, and to employ a standard form of extraction apparatus.

From the ether soluble portion of the pyridine extract of an Upper Silesian coal, after the removal of basic, phenolic, and acid substances with dilute sulphuric acid and dilute caustic soda solutions respectively, F. Hofmann and P. Damm[3] obtained neutral substances which on distillation *in vacuo* yielded fractions in which resinous substances and hydrocarbon bodies were identified. Among the hydrocarbons were members of the series C_nH_{2n-4}, C_nH_{2n-6}, C_nH_{2n-8}, and C_nH_{2n-10}.

In a chemical investigation of banded bituminous coal Tideswell and Wheeler[4] extracted with pyridine the four constituents: vitrain, clarain, durain, and fusain, with the following results:—

	Vitrain.	Clarain.	Durain.	Fusain.
Extract, per cent. on ash-free, dry coal	34·4	27·2	21·6	10·1
Colour of solution	Dark red.	Dark red.	Brownish red.	Brown.

A weighed portion (one gram) of each of the dried extracts of vitrain, clarain, and durain was extracted with chloroform during two days, and the percentage of the pyridine extract soluble in chloroform was with vitrain 27, with clarain 30, and with durain 40. From these results the figures given below were calculated.

	Vitrain.	Clarain.	Durain.
α-Compounds (insoluble in pyridine) . . .	65·8	72·8	78·4
β-Compounds (soluble in pyridine, but insoluble in chloroform)	25.0	19·0	13·0
γ-Compounds (soluble in both pyridine and chloroform)	9·2	8·2	8·6

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[1] *J.C.S.*, 1914, Vol. 105.

[2] *Proc. Roy. Soc.*, 1919, A, 96, 119–136.

[3] *Brennstoff-Chem.*, 1922, 3, 73–79, 81–91. See also *J.S.C.I.*, May 15th, 1922, p. 318A.

[4] *J.C.S.*, 1919, Vol. 115, 619–636.

These workers also submitted vitrain and durain to direct extraction with chloroform and with ethyl alcohol, and clarain with ethyl alcohol only, and the results of these extractions are shown under :—

Extract, per cent. on ash-free dry coal—

	Vitrain.	Clarain.	Durain.
Obtained with alcohol	6·6	5·7	3·1
Obtained with chloroform	2·85	—	2·4

Some very important work on the action of solvents on coal has been carried out by W. A. Bone, A. R. Pearson, E. Sinkinson, and W. E. Stockings during an investigation on the resinic constituents and coking propensities of coal.[1] Resin-solvents, such as ethyl ether, acetone, ethyl alcohol, chloroform, tetrachlorethane, trichlorethylene, benzene, and xylene, were used, and in order to avoid the action of atmospheric oxygen the extractions were carried out in an atmosphere of nitrogen.

Two series of experiments were carried out with seven coals, using in one case acetone (b.p. 56·5° C.) and in the other benzene (b.p. 80·4° C.). The experiments were carried on until no appreciable further extraction took place. The figures given below are the percentage amounts of extract obtained from the dried coal.

Coal Solvent—	A Durham coking.	B Barnsley	C Spanish	E Spanish	F South Wales	G South Wales
Acetone .	2·38	2·66	1·40	0·66	0·67	0·68
Benzene .	3·27	1·86	2·04	1·25	1·18	0·93

These extracts consist, at least in part, of coal resins, and in order to test the validity of the commonly accepted theory that the coking power of coals depends on their resinous constituents, Bone and his co-workers carried out coking tests on the residues obtained after the extraction of the above coals and found their coking propensities were unimpaired. To remove any doubt in this matter both A (Durham coking) and B (Barnsley) coals were submitted to a more drastic extraction. In each case the coal was extracted successively with (*a*) ethyl ether (eleven days), (*b*) ethyl alcohol (nine days), and (*c*) benzene (fifteen days). The results of the experiments are set out below :—

Coal	A Durham coking.	B Barnsley.
Ethyl ether (eleven days) . .	2·20	2·34 per cent. extracted.
Ethyl alcohol (nine days) . .	2·43	1·88 ,, ,,
Benzene (fifteen days) . .	2·00	0·89 ,, ,,
Total . .	6·63	5·11 ,, ,,

In this case also the residues (after drying in an atmosphere of nitrogen) were found to possess unimpaired coking properties.

The well-known fact that the coking power of coals is destroyed after extraction with basic solvents such as pyridine is mentioned, and it is pointed out that this is due rather "to the depolymerising action of the pyridine upon the coal substance" than to the removal of resins. It was found that the resin solvent tetrachlorethane attacks and decomposes the coal substance and destroys the coking power. Four coals were extracted with chloroform with the following results :—

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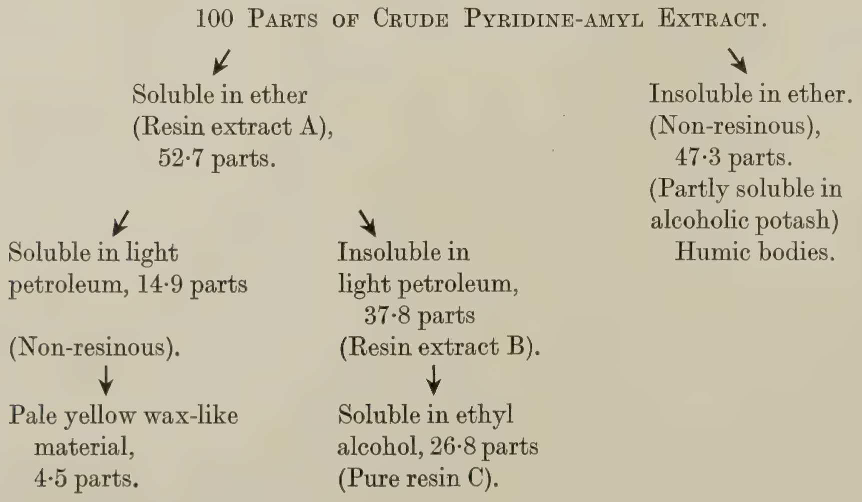
[1] *Proc. Roy. Soc.*, 1922, A, 100, 582–598. See also *Gas World*, Coking Section, April 1st, 1922, pp. 16–20.

Coal	Percentage of extract.
A (Durham)	3·27
B (Barnsley)	5·13
D (Spanish)	3·48
F (Welsh)	1·20

In each case the coking power of the residue was unimpaired. It was found, however, that if a stream of chloroform vapour was passed over the Durham and Spanish coals at temperatures between 220° and 270° C., hydrogen chloride was evolved (the coal substance was being attacked), and the coking power of the Durham coal had deteriorated somewhat, whilst that of the Spanish coal was entirely destroyed.

With the object of isolating a sufficient quantity of coal resins for a thorough examination of them a process was devised which minimised the depolymerising action of pyridine upon the non-resinous matter. A mixture of equal volumes of pyridine and amyl alcohol gave the best results. The extraction of the coal was carried out in an atmosphere of nitrogen, and at the end of the operation the solution was separated from the residue by filtration, preferably by means of an alundum cylinder. A portion of the mixed solvents was removed by ordinary distillation, and the remainder under a pressure of 20 m.m. The crude pyridine-amyl extract obtained from the Barnsley coal (B) was, by a special treatment, separated in the products shown in the following scheme :—



100 PARTS OF CRUDE PYRIDINE-AMYL EXTRACT.

Soluble in ether
(Resin extract A),
52·7 parts.

Insoluble in ether.
(Non-resinous),
47·3 parts.
(Partly soluble in
alcoholic potash)
Humic bodies.

Soluble in light
petroleum, 14·9 parts
(Non-resinous).

Insoluble in
light petroleum,
37·8 parts
(Resin extract B).

Pale yellow wax-like
material,
4·5 parts.

Soluble in ethyl
alcohol, 26·8 parts
(Pure resin C).

Only two coals were worked upon in this series of experiments, viz. Durham coking and Barnsley, and the yield of resin extract A from these coals varied from 1·27 to 2·75 per cent. of the weight taken.

The wax-like substance on purification with sulphuric acid yielded a pale yellow material with the appearance of a soft paraffin. It was soluble in ether, chloroform, and most other organic solvents, and its solutions showed a green fluorescence. Bromine was not absorbed by it. The amount obtained was approximately 0·35 per cent. of the original coal. Its ultimate composition was found to be as follows :—

	Per cent.
Carbon	86·00
Hydrogen	10·80
Oxygen (by difference)	3·20
	100·00

The pure resin C. was a translucent material deep red in colour, possessing a conchoidal fracture and producing an amber-yellow powder when crushed. Ethyl ether, alcohol, acetone, acetic acid, chloroform, and benzene dissolved it completely, but in light petroleum it was insoluble. At a temperature just above 100° C. it began to soften. It resembles a " resene " in its chemical inertness. Two determinations of its molecular weight gave (1) 453·0 and (2) 450·7. The ultimate composition and these values agree with the empirical formula, $C_{31}H_{32}O_3$.

	Found	Calculated for $C_{31}H_{32}O_3$ (M.w. 452)
Carbon	82·15	82·30 per cent.
Hydrogen	7·11	7·08 ,,
Oxygen (by difference)	10·74	10·62 ,,
	100·00	100·00

The total amount of the purified resin isolated from the two coals used in the experiments was not much greater than 1 per cent. of their weight.

The humic substances in the case of the Durham coal amounted to about 4 per cent. of its weight. The ultimate composition of the dried material is given under :—

	Per cent.
Carbon	76·25
Hydrogen	5·15
Oxygen, with little sulphur (by difference)	16·85
Nitrogen	1·75
	100·00

Attention is given to the humic substances of coal in another portion of this chapter (see page 48).

According to S. R. Illingworth[1] as the carbon : hydrogen ratio of coal increases so does the solvent action of the pyridine decrease; coals possessing a C/H ratio greater than 21 are practically unattacked by pyridine at its boiling point. If the temperature of extraction is increased there is a marked effect on the solvent action of the pyridine, and this suggests that the depolymerising action of this solvent is greatly increased as the temperature rises. The minimum temperature necessary for obtaining maximum depolymerisation varies with every coal, and the period of heating also plays a part in the action of depolymerisation.

Illingworth finds that of all the solvents usually employed for the resolution of coal, phenol possesses the greatest depolymerising action, and considers that this property, coupled with the ease with which it can be manipulated, makes it the most suitable solvent. The solvent action of phenol is very vigorous in the initial period of an extraction process, but complete extraction requires a very considerable period, owing to the presence in the coal of substances of high C/H ratio.

Up to the present the results obtained by extracting coal with various solvents are not of a very striking nature, but the fact cannot be overlooked that the more recent work has supplied some very useful data, and is full of encouragement to future investigators. Methods have been devised by which the coal substance can be separated into two main groups, viz. cellulosic (humic) and resinic, and hydrocarbon bodies (saturated and unsaturated), and resinous bodies have been isolated, which indicates that these compounds exist in the free state in many types of coal.

When dealing with "rosin" (colophony) (page 15), it was mentioned that Russell, on placing this substance on a sensitised plate in the dark and leaving it for some time, found that it reacted in such a manner that when the plate was developed an image was obtained. Also it has been pointed out that resinous bodies have been discovered in coal both microscopically (page 22) and by methods of extraction (page 34). Now, it is common knowledge that colophony is a resin and also a plant product, and if coal and also the resinous bodies extracted from it behave in a similar manner to this substance when placed on a photographic plate in the dark, then it is quite reasonable to consider it at least a partial proof of the presence of types of resin in coal; and it will also add a little more to the evidence that coal is of plant origin.

Taking a small piece of coal, after polishing one of its surfaces, Russell[2] placed it on a photographic plate and left it for sixteen hours, enclosed in a dark box, and at a temperature of between 40° and 50° C. He afterwards developed the plate and found that the structure of the coal was shown up as patches and streaks of different intensities. Like results were obtained by experimenting with all ordinary coals. This worker[3] also experimented in a similar manner with different parts of plants, resinous woods, other kinds of woods, and plant juices, and obtained images similar to those secured when working with coal.

Platt and Wheeler,[4] by the use of the same method, were able to show that cellulose has no action on a photographic plate, and concluded that the substance in the coal which affects the plate must be that portion of the pyridine extract of coal which contains resinic matters. These workers prepared from a bituminous coal a pyridine extract, and from this a portion soluble in chloroform ; retaining the residue. The dried extracts, residue, and a portion of that part of the original coal which was insoluble in pyridine, were then finely ground, and four thinly spread patches placed on the same sensitised plate. The prepared plate was then kept, at a temperature of 40° C., in a specially constructed light-tight box for twelve hours, after which it was developed. The result was as follows : The portion of the original coal insoluble in pyridine showed a very faint image ; the pyridine extract had produced a strong image of the same size and shape as the patch of powder ; the portion of the pyridine extract soluble in chloroform had produced a very strongly marked image surrounded by an extensive " halo " ; and the residue, *i.e.* that portion of the pyridine extract insoluble in chloroform, showed no image. They concluded from this that the chloroform extract contained the resinic constituents of the coal.

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[1] *Fuel*, 1922, 1, 213–218.

[2] *Proc. Roy. Soc.*, 1908, B, 80, 376–380.

[3] *Proc. Roy. Soc.*, 1906, B, 78, 385–390.

[4] *Trans. Chem. Soc.*, 1913, 103, 1713–1715.

Sinkinson[1] determined the effect of high temperatures on the stability of the constituents of the coal that can react on a photographic plate in the dark. The coals examined were Manvers Main ; Hamstead, and the ingredients of it, viz. durain, clarain, and vitrain ; Spanish coking ; and Spanish non-coking. In regard to the Manvers Main coal, samples were carbonised at 300° C., 500° C., 700° C., and 1000° C., and a portion of each residue, coarsely ground, and also of the dry and wet coal before carbonising, placed on a photographic plate, each portion being covered with an inverted porcelain crucible. The plate was enclosed in a light-tight box and kept at 40° C. for twenty-four hours. The results were as follows :—

(1) The most intense image was given by the dry uncarbonised coal, the image produced by the wet sample being slightly less in comparison.
(2) The residue from the sample carbonised at 300° C. showed less action, and that from the sample heated at 500° C. produced only a very slight image.
(3) The residue obtained from the carbonisations at 700° C. and 1000° C. showed no action at all.

Dealing with the Spanish and Hamstead coals and the separate ingredients of the latter coal, all, when carbonised at 450° C., gave images on a photographic plate, but at 500° C. the effects were not so intense. For a carbonising temperature of 550° C. there was no effect in the cases of the two Spanish coals and durain ; the effect in the case of the Hamstead coal was just perceptible, and with vitrain and clarain rather more so. At 450° C. vitrain gave the most intense image, whilst clarain came next.

The effects of durain, clarain, and vitrain on photographic plates were investigated by Stopes,[2] and she found that vitrain produced the strongest image.

By the use of a solvent made of equal volumes of pyridine and amyl alcohol,

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[1] *Jour. Chem. Soc.*, 1920, 117, 165–170.

[2] *Proc. Roy. Soc.*, 1919, B, 90, 470.

Bone and his co-workers[1] obtained an extract from which, on further treatment with solvents (see pages 36–37), they were able to isolate a pure resinous substance. This on examination was found to resemble a " resene " in its chemical inertness, and this fact coupled with the facts (*a*) that Sinkinson and Bone, in an unpublished research,[2] found that the resene portion of pure resin did not affect a photographic plate in the dark, and (*b*) that resene was the only resinous body which Bone and his co-workers obtained from the coals they worked upon (Durham and Barnsley), appears to contradict the conclusion come to by other investigators that the resinous bodies of coal are the substances which act on a photographic plate.

In a paper appearing shortly after that of Bone's (just referred to), Wheeler and Wigginton[3] claim that there is little doubt that true resins (mixtures of resin esters, resin acids, and resenes) occur in bituminous coal. There is some difference between the behaviour of the resins occurring in bituminous coals and those of modern formation, the former having undergone changes which have caused them to lose to a large extent their solubility in ether, alcohol, etc. Substances with the appearance of resins occur in some British bituminous coals in the form of layers, and these on testing prove to be true resins.

It is worthy of note that those substances in coal which affect a photographic plate in the dark are readily oxidised. Referring to vitrain, clarain, and durain, Tideswell and Wheeler[4] state " all three absorb oxygen to a marked degree, but there is a decrease in absorptive power in the order vitrain, clarain, durain, which is particularly marked at low temperatures. . . . The difference in absorptive power evinced by ' these three banded constituents of bituminous coal ' would be in their physical structure—in their power of physical absorption." Of these three constituents " the bright ones, vitrain and clarain, show greater liability to oxidise and to ignite than the dull durain."

Eric Sinkinson[5] is of the opinion that the absorption of oxygen by coal is a part of the mechanism of its action on a photographic plate, and he points out that in the presence of nitrogen or in a vacuum there is no action. It was tentatively suggested by Russell that the formation of hydrogen peroxide may be responsible for the production of an image on a photographic plate.

It should be clearly understood that molecular oxygen is not directly responsible for the effect on a photographic plate; silver bromide is not affected by this element. This salt, as is well known, is affected by the action of light, a photochemical reaction takes place, with the result shown in the following equation :—

$$4AgBr=2Ag_2Br+Br_2$$

or in the presence of gelatine, which renders the reaction irreversible :—

$$4AgBr+\text{gelatine}=2Ag_2Br+\text{brominated gelatine.}$$

Now, what is it that produces the same effect *in the dark* and in the presence of oxygen, when a piece of resin from wood or coal is placed on a photographic plate ?

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[1] *Proc. Roy. Soc.*, 1922, A, 100, 582–598.

[2] See *Jour. Chem. Soc.*, 1920, 117, p. 170.

[3] *Fuel*, 1922, 1, 10–14.

[4] *Jour. Chem. Soc.*, 1920, 117, 794–801.

[5] *Jour. Chem. Soc.*, 1920, 117, 166.

Mr. W. F. Block, an assistant of the late Dr. Russell, gives among other statements[1] (especially in reference to woods, although coal and resin were experimented with as well) the following :—

(*a*) " On the evidence the active bodies (in regard to effect on a sensitised plate) must be regarded as an emanation, but differing entirely from radio-active emanations."

(*b*) " The action takes place slowly at ordinary temperatures (one day to twenty-one days) according to the nature of the specimen, but rapidly at 50–55° C. (half to eighteen hours)."

(*c*) " The shorter exposures give sharper pictures, which observation accords with the conclusion that the active body is of the nature of a vapour or volatile compound."

(*d*) " The activity of woods is increased in all cases by exposure to strong light, and observations on the spectrum showed that the blue end was particularly active."

(*e*) " The increased activity disappears on keeping the specimens after exposure in the dark."

(*f*) " Resinous substances extracted from a number of woods were found to be more or less active. Para-abietic acid was . . . found to be particularly active. It is well known that this body shows the phenomenon of autoxidation. . . ."

(*g*) " Experiments in which the active substance in sufficient mass was swept with a stream of air, and the current of air afterwards made to act upon a photographic plate at some distance, showed that the active substance could be carried forward."

From these remarks and those of other observers it will be seen that the phenomenon under discussion is undoubtedly difficult of explanation, and in order to clear the matter up further research is necessary. As already stated, the change of the silver bromide in the gelatine of a photographic plate into a subsalt (when taking a photograph) is the result of a photochemical reaction, and it seems that the same type of reaction is responsible for the images produced on a sensitised plate by coal, coal extracts, wood resins, etc. It is well known that waves of ultra violet light affect a photographic plate, and that these waves are invisible to the eye, and it seems quite reasonable to suppose that waves of similar vibrations are produced in the cases under discussion, and that these are responsible for the change in the silver bromide molecule, and, therefore, the production of the image on the plate. Up to the present it has been demonstrated that the presence of oxygen is necessary, and that the substances must possess the property of undergoing autoxidation to a greater or lesser extent. Substances which undergo autoxidation appear to adsorb oxygen (as much oxygen is rendered " active " as is taken up by the material under oxidation), and when adsorption of a gas by a surface takes place, the latter becomes electrically charged and the former activated. Is it the electrons of the activated oxygen which set up these high frequency waves ? Emission (or absorption) of radiation is due to the electron passing from one equilibrium state to another (Bohr), and the waves emitted by the electron are waves of ultra violet light.

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[1] See *Wood Pulp and its Uses*, Cross, Bevan & Sindall, pp. 71–75. Constable & Co., London.

In the fall of the year 1922 there appeared in the public press the startling statement, " Petrol from coal—Claims for a new process," and upon reading the paragraph it indicated that Dr. F. Bergius, a German research chemist, had produced a simple process by which coal could be changed, by the use of hydrogen at a high pressure, into an oily liquid which would yield petrol or other kinds of mineral oil.

Undoubtedly this press notice referred to the process of hydrogenation of coal, a subject which is receiving increased attention as time goes on. This matter has been dealt with chiefly by Dr. Bergius, F. Fischer and H. Schrader, and F. Fischer and H. Tropsch. Apparently the Bergius process is to treat coal in suitable autoclaves at 400° C. with hydrogen at high pressures. Bergius states that he obtains his best results by using what he terms soft natural coal, and undoubtedly by this he means the lignites and brown coals. The amount of conversion into liquid fuel runs out at about 90 per cent. of the weight of the coal taken.

In the author's opinion this result seems rather high, for it allows only 10 per cent. to cover the ash, wood cells, medullary ray-cells, cuticles, and other unchanged plant substances, and also the substances which will not react with hydrogen. It should be noted that the ash in dried lignites and brown coals varies between 2·4 and 42 per cent.

It appears that Bergius has also treated heavy tar oils with hydrogen under the same conditions and obtained light oils and pitch from these materials, his average figures being 80 per cent. by weight of the original material of the former and 20 per cent. of the latter. At the present time heavy tar oils can find a ready market for the very useful purpose of assisting in the conservation of timber, so why put them through several processes and so degrade 20 per cent. by conversion into pitch ?

In the press paragraph referred to above it states that the Bergius process " would enable a large part of the British coal reserves to be transmuted into liquid fuel, would secure this country against any risk of a liquid fuel famine, and enable it to make its own oil at home." Statements of this description are distinctly misleading, and it is a pity the general public are not sufficiently educated in matters of science to understand the stupidity of them. The process of hydrogenation of coal is all very well in a way so long as lignites and brown coals are the only types dealt with, but we are not in a position to lose our source of benzene, toluene, naphthalene, anthracene, phenols, etc., which are so necessary to the coal tar colour and other industries, by subjecting the bituminous coals (humic coals) to the same process. It would be far more sensible if, as Dr. F. M. Perkin[1] has suggested, all the coal employed for domestic purposes were to be partially carbonised and the yield of crude oil obtained used for fuel purposes. This worker has pointed out that if this yield be reckoned at the very low rate of 20 gallons per ton, the production of oil per annum would be between 700,000,000 and 900,000,000 gallons. Let it not be forgotten that at present all this oil, together with other valuable coal-tar products, is being wasted by burning in the domestic grate ; and with this waste the atmosphere of towns is polluted, a factor which not only affects the health of the population, but contributes largely to the disintegration of the stone work of public and other buildings, some of which are works of art.

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[1] " Production of Oil from Mineral Sources," *Jour. Inst. Petroleum Tech.*, 5, 75–93. 1919.

A plant to deal with the Bergius process, having a capacity of sixty tons per day, has been erected at Rheinau, near Mannheim.

The hydrogenation process such as applied to coal might be quite a satisfactory method for dealing with the peats, and research in this direction is desirable.

Fischer and Schrader,[1] in their process of hydrogenation of coal, used sodium formate instead of molecular hydrogen under pressure, and state that coal is affected very little if it is treated by the latter method. According to these workers the nascent hydrogen liberated by the decomposition of sodium formate has a marked effect, not only on coal but on peat and fresh plant substances. Their researches were carried out chiefly with a Rheinish lignite. This material, if destructively distilled, yielded about 7 per cent. of its weight of tar reckoned on ash-free lignite ; but if the process was repeated after being mixed with four times its weight of sodium formate, the yield increased to between 23 and 27 per cent. A still further increase was obtained (45 per cent. of tar) by heating in an autoclave under the pressure of steam and the gases formed during the process, mixing in the first place the lignite with double its weight of sodium formate. If the lignite was mixed with eight times its weight of sodium formate and treated in an autoclave as just described, the amount of tar obtained was 48 per cent. The best temperature to use appeared to be 400° C. The yield of tar varied according to the kind of coal employed, decreasing in amount as the series of lignites, cannels, bituminous and anthracitic coals were passed through.

The subject of hydrogenation of coal has been taken up by F. Fischer and H. Tropsch,[2] but instead of using hydrogen or sodium formate they employed hydriodic acid. Experimentally they took 2 gms. of coal and heated it for 12 hours at 200° C. with 5 c.c. of hydriodic acid (sp. gr. 1·7) and 2 gms. of red phosphorus and obtained bitumen-like substances of high molecular weight soluble in chloroform. If they used higher temperatures they obtained under certain conditions petroleum-like substances. Apparently by using the method just described they did not obtain liquid products, for the substances which dissolved in chloroform on the removal of this solvent remained as a light brown powder which softened above 100° C. There is one point of interest in regard to this process which confirms the results obtained by other methods of hydrogenation, and that is coals, such as lignite and cannel, are much more easily hydrogenated than the bituminous and anthracitic coals, but the products are very similar although less in quantity with the latter types of coal. A table given by Fischer and Tropsch constructed from the results of some of their experiments bears this out :—

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[1] *Brennstoff-Chem.*, 1921, 2, 161–173. See also *J.S.C.I.*, 1921, p. 457A.

[2] *Chem. Zentr.*, 1919, 90, IV, 471–472. *Ges. Abhandl. zur Kenntnis der Kohle*, 1918, 2, 154–159. See also *J.S.C.I.*, November 29th, 1919, 855A.

Kind of Coal.	Fixed carbon in Coal.	Matter Soluble in Chloroform.	
		Before treatment.	After treatment.
	Per cent.	Per cent.	Per cent.
Anthracite . .	89	0·52	12·1
Semi-bituminous .	85	0·55	12·7
Bituminous . .	78	0·71	54·6
Flaming gas . .	64	1·5	70·3
Cannel . . .	58	2·7	73

With the object of gaining knowledge of the composition of coal some workers have resorted to the use of reagents, submitting the coal substance to the action of such materials as nitric acid, a mixture of nitric and sulphuric acids, sulphuric acid, a mixture of nitric and hydrofluoric acids, acetic anhydride, oxygen, ozone, and the caustic alkalies. To a very large extent the results obtained have been disappointing.

E. Fremy[1] submitted the higher coals (bituminous coals) to the action of a mixture of nitric and sulphuric acids with the result that they were completely broken down, a deep brown solution being obtained from which, on the addition of water, colouring matter was precipitated. In all probability this was a mixture of ulmic compounds. This worker also attempted to distinguish between lignites and bituminous coals by treating them with solutions of alkaline hypochlorites, but without success.

On treating finely divided coal with nitric acid, Guignet[2] obtained oxypicric acid $(NO_2)_2[4,6]C_6H_2[1,3](OH)_2$. The significance of this is doubtful. Oxypicric acid is isodinitro-resorcin, a resorcinol derivative, and the latter substance can be obtained from certain plant resins by treating them with potash. This worker noted also the presence of oxalic acid and a residue of nitrated products, which, on heating, behaved somewhat like nitrated cellulose.

By gently heating a Wigan cannel coal with dilute hydrochloric acid in which potassium chlorate had been dissolved, Cross and Bevan[3] found that it became soluble in alkalies, and from the alkaline solution obtained chlorinated ulmin-compounds similar to chlorine derivatives of the sugar ulmins. Smythe[4] also experimented with this reagent and obtained results of a somewhat similar nature.

Hilpert, Keller, and Lepsius[5] treated a bituminous coal from the Osterfeld mine with several reagents, among them being acetic anhydride and zinc chloride, a mixture of nitric and sulphuric acids (1 : 1), and fuming sulphuric acid. The nitrated coal was found to be partially soluble in acetone and acetic acid, but insoluble in benzene and other hydrocarbons. It was also soluble in aqueous solutions of the alkalies with partial saponification. The experiments with fuming sulphuric acid gave negative results as regards the formation of sulphonic acids, and upon the non-formation of these bodies and the ease with which the nitro products were saponified these workers concluded that aromatic hydrocarbons were absent in the coal. The results of these experiments do not appear to have thrown much light on the problem of the constitution of coal.

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[1] "Recherches chimiques sur les combustibles minéraux," *Compt. Rend.*, Vol. 52, pp. 114–118. 1861.

[2] "Sur la constitution de la houille," *Compt. Rend.*, Vol. 88, pp. 590–592. 1879.

[3] *Phil. Mag.*, Ser. 5, Vol. 13, pp. 325–328. 1882.

[4] "Report of Committee of British Association on the Proximate Constituents of Coal," 1896, 340.

[5] *Ges. Abhandl. zur Kenntnis der Kohle*, 1917, 1, 22–25. ; *Chem. Zentr.*, 90, 11, 441–442. See also *J.S.C.I.*, June 30th, 1919, p. 399A.

The banded constituents of a coal from the Top Hard seam of East Kirkby Colliery were submitted to the action of concentrated nitric acid containing a little anhydrous hydrofluoric acid by A. Baranov and W. Francis.[1] After treatment the acids were neutralised with a concentrated aqueous solution of potassium hydroxide, and then a large excess of water rapidly added. It was found that the whole of the vitrain went into solution, a dark brown, almost black liquor resulting. Clarain yielded a solution lighter in colour, but otherwise very similar to that of vitrain, and the liquid contained transparent solid fragments in suspension, which consisted chiefly of fragments of cuticles with a few broken spore exines. Of the durain only about half was dissolved, yielding a solution of a light yellow colour. Fusain, so it appeared, was not acted upon by these reagents.

The importance of the reagent oxygen in regard to its action upon coal cannot be overlooked. It plays a very great part in the process of spontaneous combustion of coal, a study of the causes of which is a matter of practical necessity, and by making careful observations on its reactions with the coal substance a considerable amount of light will be undoubtedly thrown upon the constitution of coal.

In a series of experiments Dennstedt and Bunz[2] traced a relationship between the presence of ulmin-compounds in a coal and its liability to spontaneously ignite.

Platt discovered that during the oxidation of coal one group of compounds behaves in a similar manner to carbon, a loosely combined, physico-chemical complex being formed, which breaks up and yields carbon monoxide and carbon dioxide when the temperature is raised a few degrees only. It appears that the type of compounds in coal which react thus with oxygen occur in the "cellulosic" group, and they are oxygenated compounds. It has been pointed out by several investigators that, generally, coals of a high oxygen content show greater liability to spontaneously ignite.

It has been suggested by Graham and Hill[3] that the "cellulosic" portion of coal may be that which is responsible for spontaneous combustion of coal.

When both carbon and coal are oxidised benzenehexacarboxylic acid (mellitic acid) is formed, and this indicates that in both of these substances there are molecules present of a six-carbon ring structure, each carbon atom of which is attached to an additional carbon atom. This seems to indicate that in coal there are substances the molecules of which are similar in type to the carbon molecule. In a paper on "The Oxidation and Ignition of Coal," by R. V. Wheeler,[1] this worker states: "If it is correct to assume that the similarity in behaviour towards oxygen evinced by bituminous coal and carbon is due to the presence in the coal of groups of compounds, the molecules of which have aromatic structures resembling those of the carbon molecule, it follows that the greater the proportion of such groups of compounds in a coal the greater will be the ability of that coal when newly-won to 'attach' oxygen, and the higher will be its proportion of oxygen when saturated," and further: "What is known of the constitution of coal points to the major portion of the oxygenated compounds normally present being compounds arising from the degradation of the celluloses and compound celluloses of the cell-walls of the coal-plants. It is just these compounds of which the structures of the molecules approximate most closely in character to those of carbon, which, therefore, may presumably act like carbon in causing a loose attachment of oxygen. A coal rich in such compounds—oxygenated compounds—might, therefore, be expected to absorb oxygen readily, and, *ipso facto*, to self-heat readily."

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[1] *Fuel*, 1922, 1, 219–222. See also *J.S.C.I.*, January 19th, 1923, p. 41A.

[2] "Die Gefahren der Steinkohle," *Zeits. Angew. Chem.*, Vol. 25, pp. 1825–1835. 1908.

[3] *Trans. N. Eng. Inst. Min. Eng.*, 1918, 68, 37.

J. R. Partington[2] considers that oxygen does not form compounds with the coal substance, but is merely adsorbed, and he holds that the evidences of adsorption are (*a*) a rapid initial rate of absorption, followed by (*b*) a slow and continuous absorption, and (*c*) the difference shown between moist and dry air. Wheeler and Tideswell[3] do not agree with this investigator, and point out that the rate of absorption of oxygen by coal increases with rise of temperature, whereas if it were an adsorption process there should be a decrease in the rate.

Portions of the four ingredients (vitrain, clarain, durain, and fusain) from the Hamstead thick coal were subjected to the action of air or oxygen at different temperatures by F. V. Tideswell and R. V. Wheeler,[4] with the object of determining their rates of oxidation and relative ignition temperatures, and to add data which would be of service to the general research on the mechanism of the reaction between oxygen and the coal conglomerate. The general conclusions drawn from the experiments by these investigators are:—

(*a*) "Of the three main ingredients of the banded coal, the bright ones, vitrain and clarain, show greater liability to oxidise and ignite than the dull durain. The difference between these ingredients is not, however, so great as to warrant any suggestion that the bright portions of the Hamstead coal are primarily responsible for its liability to spontaneous combustion."

(*b*) "The influence of fusain is uncertain. Many practical miners consider that spontaneous combustion originates where 'mother-of-coal' (fusain) abounds." It is "improbable that fusain has a preponderating influence in determining the actual ignition of the coal after self-heating has begun; but it is conceivable that the rapid absorption of oxygen by

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[1] *J.C.S.*, Vol. 113, 945–955. 1918.

[2] *Chem. News*, 1919, 118, 50.

[3] *J.S.C.*, 115, 895. 1919.

[4] *J.C.S.*, 117, 794–801. 1920.

> fusain at low temperatures may be attended by a sufficient evolution of heat to raise appreciably the temperature of the main mass of the coal, thereby causing the most inflammable ingredient (vitrain) to react more readily with oxygen."

The results of the experiments carried out by these workers also suggest that oxygen is first of all physically absorbed, and then gradually disappears owing to chemical reaction and formation of an oxygen complex, and that this dual process varies to a certain extent in degree and probably also in nature, as between one ingredient of the coal and another.

Fischer and Niggemann[1] carried out some experiments upon coal with the object of producing soluble products, using ozone as the reagent. These investigators suspended the coal in water and exposed it for twenty hours to the action of ozone, and found that the products obtained were easily soluble in water and alcohol, but slightly soluble in other neutral solvents. They were black or brown in colour, strongly acid in reaction, absorbed moisture from the atmosphere, were brittle at the ordinary temperatures, but became soft at 100° C., with decomposition at about 110° C., liberating carbon dioxide. They possessed odours somewhat similar to caramel. On account of the fact that cellulose and charcoal were only slightly attacked by ozone and the products obtained were of a different character to those just mentioned, these workers considered that the reactivity of coal to ozone is characteristic of the humous substances contained therein. They found that peat gave a smaller yield of products than lignite; the yield from cannel coal was somewhat larger, and that from anthracite amounted to 48 per cent. after treatment with ozone for 300 hours.

Fischer and Niggemann also observed that coals free from bituminous constituents behave towards ozone in a similar manner to that of raw coal, and they conclude that the bituminous matter is not the constituent which becomes water soluble.

The effect of subjecting coal to the action of the hologens has been a subject of enquiry, the object being to determine the presence of unsaturated compounds in the coal substance. Fischer[2] used bromine in his experiments, and found that this element was absorbed by different coals in varying amounts. Hart,[3] who used iodine, obtained very similar results.

Tideswell and Wheeler[4] experimented with iodine on the four ingredients of banded coal, using both Wijs' solution (iodine chloride in solution in glacial acetic acid) and iodine dissolved in aqueous potassium iodide solution. They found that the coal ingredients absorbed iodine very slowly, that it was impracticable to determine the maximum amount of iodine that can be absorbed by coal, because the amount absorbed varied with the conditions and more particularly with the length of duration of test, and that a portion of the iodine removed from the iodine solution by the coal was not in a state of combination but adsorbed. They also found that if Wijs' solution was used the coal absorbed about four times as much iodine as from an aqueous iodine solution in the same time. The figures given below are some of their results :—

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[1] "Conversion of Coal and Similar Substances into Soluble Products by Ozone," *Ges. Abhandl. zur Kenntnis der Kohle*, 1917, 1, 30–42; *Chem. Zentr.*, 1919, 90, 11, 442.

[2] "Selbstentzundung von Steinkohle," *Zeitsch. Angew. Chem.*, Vol. 33, 787–790. 1899.

[3] "Ein Kleiner Beitrag zur Chemie der Steinkohlen," *Chem. Zeit.*, Vol. 30, 1204–1205. 1906.

[4] *J.C.S.*, Vol. 115, pp. 622–623 and 635. 1919.

IODINE ABSORBED PER CENT. BY WEIGHT IN ASH-FREE DRY COAL.
Aqueous iodine (N/10 in potassium iodide solution).

Duration of Treatment. Hours.	Temporary (Adsorbed).			Permanent. (Chemically combined).				
	Vitrain.	Clarain.	Durain.	Fusian.	Vitrain.	Clarian.	Durain.	Fusain.
1.	6·4	7·6	4·1	0·7	8·6	6·9	6·8	2·1
3.	7·9	8·3	5·5	0·7	14·3	11·8	12·3	3·6
6.	9·3	9·7	6·8	1·4	16·5	16·0	13·0	2·9
24.	10·7	10·4	8·9	2·1	22·8	23·6	17·8	4·3

WIJS' SOLUTION

Duration of Treatment. Hours.	Temporary.				Permanent.			
	Vitrain.	Clarain.	Durain.	Fusain.	Vitrain.	Clarain.	Durain.	Fusain.
6.	18·6	20·8	17·1	8·6	67·9	63·2	51·3	4·3

The action of caustic potash on coal has been studied by a number of workers, chiefly with the object of removing from the coal substances of an acid nature (such as the resin acids) and humic or ulmic compounds. As is well known, when plant celluloses undergo disintegration by the process of " wet rot " substances of a dark brown colour, colloidal in nature, having a high specific heat and a great capacity for holding water are formed. These substances, known collectively as " humus," " humic acids," " ulmin compounds," " ulmic acids," etc., are complex in nature, and at present very little is known about them. They are soluble in caustic potash, and can be precipitated out by the addition of a mineral acid. Unfortunately, owing to the number of different terms used to describe these substances, a good deal of confusion exists, but with a view to dispelling this, present workers are adopting the term " ulmin compounds " or " ulmins."

If sugar is acted upon by dilute acids at a moderate temperature for some time " ulmins " are formed, and a number of workers have made a study of these substances. Berthelot and Andre[1] stated that the brown substance obtained when the precipitate formed by the action of dilute acids on sugar is dried at about 120° C., must be considered as a condensed or polymerised anhydride derived from the acid resulting from the change in the sugar. When subjected to the action of dilute alkalies this anhydride swells like a colloid and forms (*a*) a small amount of soluble basic salts, some of which are derived from acids more hydrated than the originally precipitated acids ; and (*b*) a smaller quantity of insoluble salts.

Maillard showed that a substance resembling " humus " is produced when sugar is heated either with mineral or amino-acids ; in the latter case the " humus " contains nitrogen. V. A. Beckley[1] investigated this matter further, and showed that sugars on treatment with acids gave rise to hydroxymethylfurfuraldehyde, and this substance readily condenses to form a substance very similar to " humus." He found hydroxymethylfurfuraldehyde in rotting straw in which " humus " was being formed. According to Beckley the formation of " humus " in soil proceeds in two stages, as shown by the following :—

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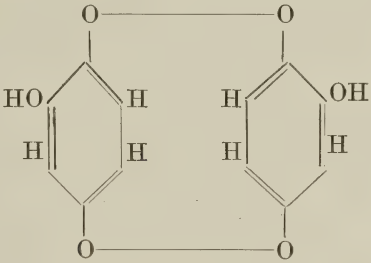
[1] " Recherches sur les humiques," *Ann. Chem. Phys.*, Ser. 6, Vol. 25, 1892.

(*a*) Carbohydrate (cellulose, etc.)+amino-acid=hydroxymethylfurfuraldehyde.
(*b*) Hydroxymethylfurfuraldehyde + amino-acid =" humus "+ furfuraldehyde $+CO_2$ by condensation.

Eller and Koch[2] suggest that " humus " is formed by the oxidation of quinones which are previously generated from the hexoses by the elimination of water. They assign to this the constitutional formula :—



This formula indicates that the acidity is due to phenolic groups ; but Sven Oden[3] contradicts this and states that his experiments indicate that the acidity is due to the presence of carboxyl groups.

Marcusson[4] contends that the " humic acids " obtained from brown coal contain condensed furan and benzene rings, and if they are not identical with, they stand in close relationship to the synthetic acids which can be prepared from the sugars.

By physico-chemical means (potentiometric titration), Sven Oden[5] proved that prepared " humic acid " and also the organic constituents of peat (after the removal of the acids soluble in water), both possess acid properties.

Detmer[6] obtained humic acid by treating peat with a solution of potassium carbonate and then adding hydrochloric acid to the solution. The precipitate was repeatedly purified, and the resulting amorphous substance on analysis corresponded to the formula $C_{20}H_{18}O_9$. It was found to contain a small quantity of nitrogen (0·179 per cent.). This worker considered " ulmic acid " to be identical with " humic acid."

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[1] *J. Agric. Soc.*, 1920, 11, 69.
[2] *Ber.*, 1920, 53 [B], 1469. See also *J.C.S.*, 1920, i, 733 (abstract).
[3] *Koll. Chem.*, *Beihefte*, 1919, 11, 75.
[4] *Z. Angew. Chem.*, 1922, 35, 165. See also *J.C.S.*, 1922, i, 436 (abstract).
[5] *Trans. Faraday Soc.*, 1922, Vol. 17, 2, 288.
[6] *Landw. Versuchs. Stat.*, 14, 248.

Mulder[1] not only carried on investigations on the sugar ulmins, but on the materials which can be extracted from peat by means of alkalies. The results of his experiments caused him to form the opinion that the sugar ulmins which he prepared and the compounds he obtained from peat were identical.

With the object of comparing sugar-ulmin with peat-ulmin, Robertson, Irvine, and Dobson[2] extracted and examined an ulmin from heather peat, and found it resembled the sugar compound closely in appearance, solubility, and general properties ; but its analysis was different : C., 56·67 ; H., 5·16 ; O., 35·68 ; N., 2·49 per cent. against C., 66 ; H., 4·5 ; O., 31·5 per cent. for the sugar-ulmin.

The investigations by Doppler[3] on the peculiar black jelly found in peat bogs, followed by those of Schrötter,[4] Haidinger[5] (who suggested the name of "Dopplerite" for the material in honour of Doppler), Von Gümbel,[6] Demel,[7] and Früh,[8] and more recently by those of Moss,[9] and in 1922 by those of F. V. Tideswell and R. V. Wheeler,[10] undoubtedly throw some light on the nature of the formation and constitution of coal.

Dopplerite is a black gelatinous substance, colloidal in nature, containing a high percentage of water (above 70 per cent.), which when dried becomes a brittle, shining black substance possessing a conchoidal fracture somewhat similar to vitrain. The fresh substance on exposure to the atmosphere loses its moisture rapidly, and becomes elastic and of the consistence of india-rubber. It is insoluble in water, sparingly soluble in alcohol and ether, but is readily dissolved by a solution of potassium hydroxide. It shows an acid reaction towards litmus, and contains, usually, a small quantity of mineral matter.

Undoubtedly dopplerite is a member of the group of substances now called "ulmic substances" or "ulmins," which result from the decay of vegetable matter, or which can be prepared from certain organic materials such as the sugars. As regards the constitution of these substances very little is known beyond the fact that the presence of certain reactive groupings in the molecule have been recognised. As with many of the colloid substances the molecules are undoubtedly large and complex. According to Berthelot and André,[11] ulmin is the anhydride of a polybasic acid, and partakes of the nature both of an acid and an alcoholic anhydride. Evidence of the presence of carboxyl groups in the ulmins is shown in the facts that on heating at a moderate temperature carbon dioxide is given off, and that they are readily esterified. It has been shown[1] that all ulmins, however obtained or prepared, yield protocatechuic acid on fusion with potassium hydroxide, which indicates the presence of the grouping—

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[1] "Untersuchungen über die Hummussubstanzen," *Jour. prakt. Chem.*, Vol. 21, pp. 203–240, 221–370. 1840.

[2] "A Contribution to the Chemistry and Physiological Action of the Humic Acids," *Biochem. Jour.*, Vol. 2, pp. 458–480. 1907.

[3] Sitzungsber, *Akad. Wiss. Wien*, 1849, 3, 239.

[4] Sitzungsber, *Akad. Wiss. Wien*, 1849, 3, 285–287.

[5] Sitzungsber, *Akad. Wiss. Wien*, 1849, 3, 287–293.

[6] *Neues Jahrbuch*, 1858, 278.

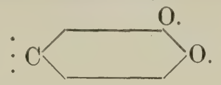
[7] Sitzungsber, *Akad. Wiss. Wien.*, 1883, 86, 872–878.

[8] Monograph entitled *Uber Torf und Dopplerite*, Trogen. Pp. 88, Pl. 1. Zurich, 1883.

[9] *Sci. Proc. Roy. Soc.*, Dublin, 1903, 10, 1, 93.

[10] *J.C.S.*, 1922, Vol. 121, 2345–2362.

[11] *Ann. Chim. Phys.*, 1892 [VI], 25, 364.



This grouping is present also in the lignone portion of the ligno-celluloses and in the tannins. Roger and Vulquin[2] investigated a peat ulmin which gave an analysis: C., 57·4; H., 3·1; N., 1·3; O., 32·8 per cent., on the presumption that its source was the ligno and pecto-celluloses, and that it contained groupings known to be present in these compounds. They were able to show that (1) pentosanes and hexosanes were absent; (2) the alcoholic properties of the celluloses were preserved, for an acetyl compound and a compound analogous to cellulose thiocarbonate could be formed; (3) various constituents of the ligno-cellulose molecule were still in existence; for example, a C_6 nucleus (as evidenced by the formation of protocatechuic acid) and a secondary acetyl constituent ($CH_2{-}CO$). The character of the unsaturated components of ligno-celluloses, capable of combining directly with the halogens, seemed also to be preserved.

In their paper on dopplerite, Tideswell and Wheeler[3] state that most of their "information regarding the constitution of dopplerite is obtained from a study of the products of decomposition by heat of the dried material," and "in general" their "examination of dopplerite shows its constitution to conform with that of the ulmins as disclosed by the work of Roger and Vulquin."

Tideswell and Wheeler fractionally distilled under vacuum portions of dried (in an atmosphere of nitrogen) dopplerite, and in one case collected and examined the gaseous products and in the other the liquid products. Table 5 gives the volumes of the principal gaseous products, and Table 6 the liquid distillation products obtained by them.

TABLE 5

VOLUMES OF THE PRINCIPAL GASES EVOLVED AT EACH TEMPERATURE PER GRAM OF ASH-FREE, DRY MATERIAL

C.C^{s}. at N.T.P.

Temperature.	0–150°	200°	250°	300°	350°	400°	450°	500°	550°	600°
Carbon dioxide .	4·8	11·0	17·6	14·7	8·4	4·2	3·0	3·0	1·5	0·3
Carbon monoxide	0·3	1·9	4·8	5·3	5·6	5·9	6·7	7·2	8·8	10·0
Hydrogen . .	—	—	—	—	—	2·0	7·2	19·2	29·1	30·6
Paraffins . .	—	—	—	0·6	2·3	3·4	5·6	4·0	2·5	1·1

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[1] Demel, "Uber den Dopplerit von Aussee," *Monat. Chem.*, Vol. 3, pp. 763–769. Wien, 1882.

Hoppe-Seyler, "Ueber Huminsubstanzen, ihre Entstehung und ihre Eigenschaften," *Zeit. Physiol. Chem.*, Vol. 13, pp. 66–121. Strassburg, 1889.

[2] Roger and Vulquin, "Contribution à l'étude des matières humiques de l'ouate de tourbe," *Compt. Rend.*, 1908, 147, 1404.

[3] *J.C.S.*, 1922, Vol. 121, pp. 2345–2362.

TABLE 6

Liquid Distillation Products

Temperature.	Aqueous Distillate.			Oils.			
	Percentages on original ash-free, dry dopplerite.			Percentages on original ash-free, dry dopplerite.			
	Water,	Ammonia,	Acids.	Bases	Phenols,	Acids,	Neutral Oils.
Up to 90° . . (Fraction A)	7·0	—	—	—	—	—	—
	(Some methyl alcohol, but no aldehydes, ketones, or organic acids.)						
Between 90° and 270° (Fraction B)	15·0	0·003	0·10	Traces	Nil	0·002	0·007
	(The acid had an equivalent 416 ; acetic acid was present, and furfural 0·036 per cent.)						
Between 270° and 410° (Fraction C)	2·5	0·002	—	Traces	Nil	0·002	0·015
	(Furfural was absent)						
Between 410° and 550° (Fraction D)	2·0	0·004	—	Not examined			
Between 270° and 550° (Fraction E)	1·7	0·040	0·01	0·02	0·65	0·023	0·30
	(Organic acids, equivalent 285, and a weak base present ; no furfural)						

Totals : Per cent. on original ash-free, dry dopplerite ; water, 28·0 ; ammonia, 0·05 ; bases, 0·02 ; phenols, 0·65 ; acids, 0·14 ; neutral oils, 0·32. "Cresols, distilling between 190–200°, were isolated from the phenolic portion of the oils, their quantity accounting for about 75 per cent. of the total phenols, which had the reactions of the simple phenols. No evidence was obtained of the presence of pyrocatechol or other of the polyhydroxyphenols."

"A saturated hydrocarbon, m.p. 45°, was isolated from the neutral oils by fractional solution and crystallisation from pentane and alcohol. The neutral oils also contained a carbohydrate decomposition product ; the remainder consisted of hydrocarbons, both saturated and unsaturated."

As has already been stated, "ulmins" are soluble in potassium hydroxide solution, and if they are present in bituminous coals then extraction with this reagent should remove them. It has, however, been found that on extracting anthracite with a solution of potassium hydroxide no "ulmic compounds" are obtained, and very little, if any, extract is yielded from the bituminous coals, whilst from the lignites fair amounts are removed, and peat yields even larger quantities. The small amounts obtained from bituminous coals does not signify that " ulmins " were not present in the early stages of the formation of coal, and that they do not exist in the coal substance in a changed form, and insoluble in alkaline solutions. Tideswell and Wheeler (*loc. cit.*) incline to the view that through polymerisation and dehydration, accompanied by the formation of anhydrides and lactones, the " ulmins " have become so changed in character that they have lost their " characteristic " solubility in alkaline solutions, and " that the amorphous cementing material for the numerous plant-structures in coal was originally a soluble ulmin, corresponding with the ulmins which surround and permeate the plant-structures in peat." These workers also call attention to the fact that the tars obtained from vitrain[1] and dopplerite are very similar, so much so that sufficient evidence exists to show that both contain the same type of structure, " a structure derived from the celluloses of the plants from which the ulmin compounds were formed."

It has been pointed out by Mahler and others that substances having all the characteristics of ulmins are produced when coal is oxidised by the oxygen of the atmosphere, and Boudouard obtained " ulmins " from bituminous coal by submitting it to the oxidising action of nitric acid.

A. R. Pearson,[2] in a recent and very instructive paper, gives the name " ultrahumin " to the non-resinic constituents of coal, and states that the pyridine insoluble portion of coal consists of α-ultrahumins and that portion soluble in pyridine, but not " resinic " constitutes the β- and γ-ultrahumins. It is interesting to note that this worker has obtained experimental evidence that pyridine is adsorbed by the ultrahumins. From the results obtained by acting upon α-, β, and γ-ultrahumins it is concluded that these bodies contain a very stable molecular nucleus, in which nitrogen is included, probably in heterocyclic combination. For all the ultrahumins obtained from the coals examined this nucleus is the same, or nearly so, and when the oxahumins (prepared by treating the ultrahumins with concentrated sulphuric acid) are brominated to saturation, the oxidised nucleus, or at least some portion of it, still survives.

The mineral constituents of coal hardly concerns this chapter, but it cannot be concluded without calling the reader's attention to an interesting and very suggestive paper by Dr. R. Lessing[3] on this subject. It is stated that the composition of the ashes of clarain and vitrain make it very probable that they represent mainly the remainder of the original plant ashes, and the presence of magnesia, especially in the ash of clarain, coupled with the fact that leaf-tissues are found in this constituent of banded coal, suggests the presence of degradation products of leaf substance containing chlorophyll.

Further knowledge of the nature of the constituents of coal substance is required, not only from the purely scientific point of view, but to enable the technologist to solve many of his difficulties in regard to the spontaneous combustion of coal, the classification and grading of coal for special purposes, the most satisfactory way in which to conserve our coal resources and obtain maximum efficiency with minimum of waste, and so on.

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[1] For particulars of these tars, see Tideswell and Wheeler, *J.C.S.*, 1919, 115, 619–636.

[2] " Some new Derivatives of Bituminous Coal," *J.S.C.I.*, 1923, Vol. 42, No. 8, 68–72T.

[3] " The Mineral Constituents of Banded Bituminous Coal," *J.C.S.*, 1920, Vol. 117, pp. 256–265.

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CHAPTER III

COAL TAR, ITS COMPOSITION, ETC.

Coal tar is such a familiar material that it is unnecessary to give a description of its appearance. It is a very complex mixture of chemical compounds, chiefly of the aromatic series. The manner in which it is prepared and the nature of the raw material (coal) influence to a wide extent its chemical composition and physical properties. Dealing first with its chief physical constant, specific gravity, this varies in practice between 1·070 and 1·215, according to the temperature of carbonisation or kind of retort employed. The lower-gravity tars are generally produced when low carbonisation temperatures are used, or if the coal is carbonised in chamber or vertical retorts. High heats in horizontal retorts produce tar of high specific gravity. Viscosity is affected in a similar manner. Reference to Tables 7 and 8 will illustrate these statements.

TABLE 7

	[1] High Heat Tar. Horizontal Retorts. Temp. approx. 1100° C.	[1] Low Heat Tar. Horizontal Retorts. Temp. approx. 800° C.	[2] Vertical Retort Tar.	[3] Chamber Retort Tar.
Specific gravity at 60° F. .	1·207	1·000	1·10 to 1·12	1·18

TABLE 8[4]

	Tar *ex* English Coal.	
	Viscosity—Engler degrees.	
	Horizontal Retorts.	Vertical Retorts.
At 20° C. . .	550·0	39·3
,, 50° C. . .	51·0	3·9
,, 70° C. . .	23·0	2·2
Specific gravity .	1·246	1·124

The absolute chemical constitution of medium and high-temperature coal tars is far from settled, and even at the present day comparatively little is known about it. During the last few years a great deal of work has been done on low-temperature tar (chiefly lignite tar), and our knowledge of the constitution of this type of tar is rapidly increasing. Consideration will be given to this subject in another place in this chapter (see page 62).

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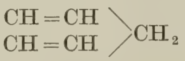
[1] Lewis T. Wright, *Jour. of Gas Lighting*, Vol. 52, p. 169.

[2] Higher figure from *Proc. Inst. Gas Eng.*, 1908, p. 130.

[3] *Gas World*, February 26th, 1910, p. 262.

[4] Dr. W. Allner. See *Jour. of Gas Lighting*, July 11th, 1911.

It is supposed that moderately high and high-temperature coal tars contain 210 or more definite chemical compounds, and from the distillates and pitch obtained when these tars are submitted to the process of destructive distillation about 120 of these compounds have been definitely isolated. Of these, 58 are hydrocarbons, 20 oxygenated compounds, 15 sulphur compounds, and 27 nitrogenous compounds. The following list gives the formulæ and some of the physical constants of the majority of these substances :—

Name.	Formula.	Sp. Gr.	Boiling Point °C.	Melting Point °C.
Hydrocarbons.				
Methane series, $C_nH_{2n}+2$				
Heptane (normal)	$CH_3(CH_2)_5CH_3$	0·712 @ 16°	97·5–98°	—97·1°
Octane (normal)	C_8H_{18}	0·7038 @ 12·5°	124°	—56·5°
Decane (normal)	$C_{10}H_{22}$	0·730 @ 20°	73°	—31°
Ethylene series, C^nH_{2n}				
Butylene (normal)	$CH_3.CH_2{\cdot}CH : CH_2$	—	—5°	—
Amylene (normal)	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH : CH_2$	—	37°	—
Hexylene (normal)	C_6H_{12}	0·6996 @ 0°	68°	—
Cyclic Hydrocarbons, C_nH_{2n}				
Naphthenes, traces in coal tar	—	—	—	—
Acetylene series, $C_nH_{2n}-2$				
Crotonylene	$CH_3{\cdot}C : C{\cdot}CH_3$	—	27°	—
Pentacarbocyclic series, $C_nH_{2n}-4$				
Cyclopentadiëne	 $\left.\begin{matrix}CH=CH\\CH=CH\end{matrix}\right\rangle CH_2$	0·815 @ 15°	41°	—
Nonone	C_9H_{14}	—	174°	—
Benzene series, $C_nH_{2n}—6$				
Benzene	C_6H_6	0·884 @ 15°	80·36°	5·48°
Toluene	$C_6H_5{\cdot}CH_3$	0·872 @ 15°	111°	—
Orthoxylene	$C_6H_4{\cdot}(CH_3)_2$	0·756 @ 14°	142°	—28°
Metaxylene	$C_6H_4{\cdot}(CH_3)_2$	0·8668 @ 19°	140°	—54°
Paraxylene	$C_6H_4{\cdot}(CH_3)_2$	0·862 @ 19·5°	138·5°	15°
Pseudocumene 1 : 2 : 4	$C_6H_3(CH_3)_3$	0·888 @ 15°	169°	—
Mesitylene 1 : 3 : 5	$C_6H_3(CH_3)_3$	0·865 @ 15°	164·5°	—
Hemellithol 1 : 2 : 3	$C_6H_3(CH_3)_3$	0·901 @ 15°	175°	—
Ethylbenzene	$C_6H_5{\cdot}C_2H_5$	0·866	137°	—
Cumene (isopropylbenzene)	$C_6H_5CH(CH_3)_2$	0·880 @ 0°	152°	—
Propylbenzene	$C_6H_5{\cdot}C_3H_7$	0·881 @ 0°	157°	—
o-Ethyltoluene	$C_6H_4(CH_3)C_2H_5$	—	—	—
m-Ethyltoluene 1 : 3	$C_6H_4(CH_3)C_2H_5$	0·869 @ 20°	158°–159°	—
p-Ethyltoluene 1 : 4	$C_6H_4(CH_3)C_2H_5$	—	161°–162°	—
Cymene 1 : 4	$C_6H_4{\cdot}CH_3.C_3H_7$	0·8722 @ 0°	175°–176°	—
Durene 1 : 2 : 4 : 5	$C_6H_2(CH_3)_4$	—	196°	80°–81°

Name.	Formula.	Sp. Gr.	Boiling Point °C.	Melting Point °C.
Isodurene 1 : 2 : 3 : 5	$C_6H_2(CH_3)_4$	—	195°	—
Series, $C_nH_{2n}-10$	C_9H_8			
Indene	$C_6H_4 \cdot C_3H_6$	1·0002	182°	—
Hydrindene	$C_{10}H_{10}$	0·957 @ 15°	176°	—
Methylindenes	$C_{11}H_{12}$	—	—	—
Dimethylindenes		—	—	—
Naphthalene series—				
Naphthalene $C_nH_{2n}-12$	$C_{10}H_8$	1·1517 @ 15°	218°	79°
α-Methylnaphthalene	$C_{10}H_7 \cdot CH_3$	1·0287 @ 12°	240°–242°	—22°
β-Methylnaphthalene	$C_{10}H_7 \cdot CH_3$	—	241°–242°	32·5°
Series, $C_nH_{2n}-14$				
Acenaphthene	$C_{12}H_{10}$	—	278°	95°
Diphenyl	$(C_6H_5)_2$	—	254°	70·5°
$C_nH_{2n}-16$				
Fluorene	$C_{13}H_{10}$	—	295°	116°
Anthracene series—				
Anthracene $C_nH_{2n}-18$	$C_{14}H_{10}$	—	351°	216·5°
Anthracene dihydride	$C_{14}H_{12}$	—	313°	106°–108°
Anthracenehexahydride	$C_{14}H_{16}$	—	290°	63°
Monomethylanthracene	$C_{14}H_9 \cdot CH_3$	—	> 360°	200°
Phenanthrene $C\ H_{2n}-18$	$C_{14}H_{10}$	—	340°	96°
Fluoranthene	$C_{15}H_{10}$	—	250° @ 60 m.m.	109°
Pyrene	$C_{16}H_{10}$	—	> 360°	148°
Chrysene	$C_{18}H_{12}$	—	436° With partial decomposition	250°
Truxene	$C_{18}H_{12}$ $(C_{27}H_{18}?)$	—	—	365°
Chrysogen	—	—	—	280°–290°
Retene	$C_{18}H_{18}$	—	350°	98°–99°
Crackene	$C_{24}H_{18}$	—	500° With decomposition	308°
Oxygenated Compounds—				
Acetone	C_3H_6O	0·792 @ 18°	56·3°	—
Acetophenone	C_8H_8O	1·032 @ 15°	200°	20·5°
Phenol	$C_6H_5 \cdot OH$	1·065 @ 18°	182·6°	42·5°
o-Cresol 1 : 2	$C_6H_4(CH_3)(OH)$	1·039 @ 23°	191°	30°–31°
m-Cresol 1 : 3	Do.	1·033 @ 19°	202·8°	—
p-Cresol 1 : 4	Do.	1·033 @ 23°	201·8°	35·5°
α-Naphthol	$C_{10}H_7OH$	1·224 @ 4°	278°–280°	94°
β-Naphthol	$C_{10}H_7OH$	1·217 @ 4°	285°–286°	122°–123°
Cumerone	C_8H_6O	—	177°	—
o-Methylcumerone	$CH_3C_8H_5O$	—	190°–191°	—
m-Methylcumerone	$CH_3C_8H_5O$	1·056 @ 16°	195°–196°	—
p-Methylcumerone	$CH_3C_8H_5O$	1·0467 @ 15°	197°–199°	—
β-Naphtholfuran	$C_{12}H_8O$	—	284°–286°	50°–51°
Diphenylene oxide	$C_{12}H_8O$	—	275°–276°	86°–87°
Dioxydiphenyl	$C_{12}H_{10}O_2$	—	235°–236°	109°

Name.	Formula.	Sp. Gr.	Boiling Point °C.	Melting Point °C.
Sulphur Compounds—				
Carbon disulphide	CS_2	1·262 @ 20°	46·5°	—
Thiophene	C_4H_4S	1·062 @ 18°	84°	—
α-Thiotolene	$CH_3{\cdot}C_4H_3{\cdot}S$	1·0194 @ 18°	112°–113°	—
β-Thiotolene	$CH_3{\cdot}C_4H_3{\cdot}S$	1·019 @ 18°	113°	—
Thioxenes (Dimethylthiophenes) several isomers	$C_4H_2S(CH_3)_2$	—	—	—
Thionaphthene	C_8H_6S	—	220°–221°	30°–31°
Diphenylene sulphide	$C_{12}H_8S$	—	332°–333°	97°
Methyl mercaptan	CH_3SH	—	6°	—
Methyl sulphide	$(CH_3)_2S$	0·845 @ 21° 0·870 @ 0°	37·5°	—
Ethyl mercaptan	C_2H_5SH	0·835 0·839 @ 0°	36·2°	—22°
Ethyl sulphide	$(C_2H_5)_2S$	0·8367 0·837 @ 0°	92°	—
Nitrogen Compounds—				
Basic—				
Aniline	$C_6H_5NH_2$	1·027 @ 12°	183°	—8°
Pyridine	C_5H_5N	0·989 @ 15°	115°	—
Picolines—				
α-Methyl-pyridine	$CH_3{\cdot}C_5H_4{\cdot}N$	0·950 @ 15°	129°	—
β-Methyl-pyridine	$CH_3{\cdot}C_5H_4{\cdot}N$	0·9771 @ 0°	140°–142°	—
γ-Methyl-pyridine	$CH_3{\cdot}C_5H_4{\cdot}N$	0·9742 @ 0°	142°–144°	—
Lutidines—				
αα′-Dimethylpyridine	$(CH_3)_2C_5H_3{\cdot}N$	0·942 @ 0°	142°	—
αγ-Dimethylpyridine	$(CH_3)_2C_5H_3{\cdot}N$	0·949 @ 0°	157°	—
αβ′-Dimethylpyridine	$(CH_3)_2C_5H_3{\cdot}N$	—	162°–163°	—
βγ-Dimethylpyridine	$(CH_3)_2C_5H_3{\cdot}N$	—	164°	—
Collidines—				
αβα′-Trimethylpyridine	$(CH_3)_3{\cdot}C_5H_2{\cdot}N$	0·9132 @ 0°	170°–172°	—
αβγ-Trimethylpyridine	$(CH_3)_3{\cdot}C_5H_2{\cdot}N$	—	165°–168°	—
Indol	C_8H_7N	—	253°–254°	52°
Quinoline (Leucoline)	C_9H_7N	1·0947 @ 20°	239°–240°	—
Isoquinoline	C_9H_7N	1·099 @ 20°	236°–237°	20°
α-Methylquinoline	$CH_3{\cdot}C_9H_6{\cdot}N$	—	238°–239°	—
γ-Methylquinoline	$CH_3{\cdot}C_9H_6{\cdot}N$	—	256°–258°	—
Acridine	$C_{13}H_9N$	—	—	110°
Non-basic—				
Pyrrol	C_4H_5N	0·966 @ 21°	130°–131°	—
Acetonitrile	$CH_3{\cdot}CN$	0·791 @ 14°	81°	—
Benzonitrile	$C_6H_5{\cdot}CN$	1·000 @ 25°	190°	—
Carbazol	$C_{12}H_9N$	—	351°	238°
Phenyl-p-naphthylcarbazol	$C_{16}H_{11}N$	—	—	330°

The chief constituents of coal tar will receive full attention in the chapters dealing with their recovery.

This chapter will not be complete unless some consideration be given, as far as possible, to the formation of tar, or rather its constituents.

During the years 1863, 1866, 1867, 1869, and 1877, Berthelot carried out a number of researches on the effect of passing vapours of hydrocarbons through red-hot tubes, and he found that the simpler hydrocarbons of the aliphatic series by the removal of hydrogen atoms and subsequent polymerisation yielded aromatic hydrocarbons. For instance, from acetylene it was possible to obtain hydrogen, ethane, ethylene, benzene, styrolene, and naphthalene; and from methane, propylene, benzene, and naphthalene. Consequently, Berthelot propounded a theory that many of the aromatic hydrocarbons of coal tar originated from acetylene by processes of condensation. In order to render the theory sound it requires that acetylene exhibits a stability at high temperatures above all other hydrocarbons, and that these latter under high-temperature conditions break down and form large quantities of acetylene, which, by condensation, are converted into various aromatic hydrocarbons. In 1908,[1] by careful experimenting, Bone and Coward were able to show that methane and not acetylene is the most stable hydrocarbon at high temperatures, and this fact proves Berthelot's theory to be unsound. However, the results of Berthelot's researches, which were carried out before anything much was known of the constitution of coal, seemed to explain in a simple manner the way in which some of the aromatic hydrocarbons occurring in coal tar were formed during the destructive distillation of coal, and for a considerable period of time this explanation claimed acceptance.

In order to consider the formation of moderately high and high-temperature tars in the light of present-day knowledge, it is necessary to study first of all the subjects of " vacuum tar " and low-temperature tar, keeping in mind at the same time what has been discovered in regard to the constitution of coal (see Chapter II and also journals, etc., referred to in the footnotes of that chapter and in the appended Bibliography). It is highly probable that most of the compounds found in high-temperature tars are produced by the decomposition of low-temperature tar compounds previously formed.

By extracting coal with boiling benzene Pictet and Ramsayer[2] obtained hydrocarbons and oxygenated compounds, which corresponded to those recovered by them from the tar (" vacuum tar ") produced when coal is distilled in a vacuum.

" Vacuum tar " is produced by distilling coal in special apparatus at a pressure not exceeding 17 m.m. mercury, and the work done on this subject by Pictet and Bouvier and also Jones and Wheeler is of considerable interest to the student.

A bituminous coal from Montrambert (Loire) was distilled at a pressure of 15 m.m. mercury by Pictet and Bouvier,[3] with the following results: The distillation commenced at about 100° C. and was completed at 450° C., and in addition to gas and coke about 1·5 per cent. of an acid liquor free from combined ammonia and 4 per cent. of tar were obtained. The tar was fluid, translucent, and of a clear brown colour with a slight green fluorescence, and its odour resembled petroleum rather than high-temperature coal tar. When freshly prepared its specific gravity was less than that of water; but on keeping it increased, and as this increase in density occurred in the absence of air, oxidation cannot be the cause of it; probably it is due to polymerisation of certain of its constituents. Phenols appear to be absent, although several bodies of an alcoholic nature (very likely hydro-aromatic alcohols), constituting about 2 per cent. of the tar, were isolated. To four of these compounds Bonner and Kaiser gave the following formulæ:—

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[1] *Trans. Chem. Soc.*, 95, 1197 (1908); *Coal and its Scientific Utilisation*, 1918, p. 140.

[2] *Arch. des. Scien. phys. et nat. de Genève*, Vol. 32, p. 514; and Vol. 38, pp. 357–423.

[3] A. Pictet and M. Bouvier, " Ueber die Destillation der Steinkohle unter vermindertem Druck," *Ber. deut. Chem. Gesell.*, Vol. 46, pp. 3342–3353.

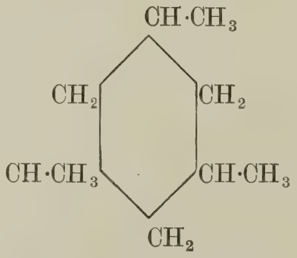
$$C_7H_{14}O,\ C_8H_{10}O,\ C_9H_{12}O \text{ and } C_{10}H_{14}O,$$

but up to the present their constitutional formulæ remain unestablished. Extraction with dilute hydrochloric acid resulted in the recovery of about 5 per cent. of basic compounds, and two of these appear to have the formulæ $C_{10}H_{11}N$ and $C_{12}H_{15}N$ respectively.

The balance of this tar consisted of a mixture of saturated and unsaturated hydrocarbons, but with the entire absence of aromatic hydrocarbons, such as naphthalene and anthracene. Among the unsaturated hydrocarbons there were in all probability none of the ethylenic type, and in a further careful examination of the hydrocarbons of "vacuum tar," Pictet and Bouvier[1] succeeded in isolating six members of the series of hydro-aromatic hydrocarbons to which they give the following properties:—

Hydrocarbon.	Boiling Point.	Sp. Gravity.	Refractive Index at the same temp.
C_9H_{18}	135°–137° C.	0·7590 @ 20° C.	1·4212
$C_{10}H_{20}$	160°–161° C.	0·7680 @ 20° C.	1·4272
$C_{10}H_{20}$	172°–174° C.	0·7765 @ 23° C.	1·4196
$C_{11}H_{22}$	189°–191° C.	0·7838 @ 22° C.	1·4234
$C_{10}H_{24}$	211°–213° C.	0·7862 @ 21° C.	1·4293
$C_{13}H_{26}$	227°–229° C.	0·7953 @ 20° C.	1·4379

The hydrocarbon C_9H_{18} they consider to be hexahydromesitylene, and to which they give the constitutional formula:—



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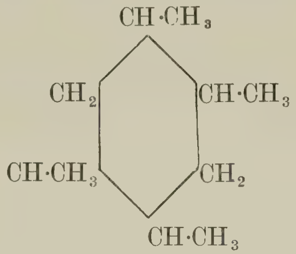
[1] *Comptes rend.*, 160, 629. See also *Ber.*, 1914, 46, 3342, and *Comptes Rend.*, 157, 1436. 1913.

identified as hexahydrodurene (1.2.4.5—tetramethyl-cyclohexane) of the constitutional formula :—



These workers[1] also obtained from vacuum tar a substance of the formula $C_7H_{14}O$, and also three aliphatic alcohols, $C_8H_{10}O$, boiling-point 185°–190° C., $C_9H_{12}O$, boiling-point 230°–235° C., and $C_{10}H_{14}O$, boiling-point 215°–220° C. On another occasion Pictet and Bouvier[2] separated from this tar a hydro-aromatic hydrocarbon of the formula $C_{30}H_{60}$, called melen, and it should be noted that this compound can be extracted from coal by boiling benzene.[3]

A sample of " vacuum tar " prepared from a bituminous coal when examined by H. Tropsch[4] gave 27·6 per cent. of a low boiling neutral oil, 40·2 per cent. of a neutral oil boiling above 150° C., 1·6 per cent. of a substance very similar in appearance to bitumen, 21·0 per cent. of phenolic bodies, 0·49 per cent. of carboxylic acids, and 0·46 per cent. of other substances which were soluble in water, and also in solutions of caustic soda.

As will be seen in what follows, the vacuum tars obtained by Jones and Wheeler[5] from a Scotch bituminous coal and also a Durham bituminous coal differed somewhat in their constituents to those of the vacuum tars obtained by Pictet and Bouvier which we have just dealt with. These differences may be accounted for, most probably, in the variations in character between English and French coals, although the methods of working and the apparatus used by these two pairs of workers varied, and these incidents may have contributed their quota.

The two coals experimented upon by Jones and Wheeler were broken into fragments which passed through a 10-mesh and remained in a 60-mesh sieve, and then dried at 105° C., after which they were distilled in a vacuum fractionally, in stages of 50° until a temperature of 430° C. was reached. Means were taken to avoid reflux condensation of the liquid products, and so prevent any risk of change in their constitution taking place. The time occupied in the distillation of each coal was about five weeks.

The aqueous liquor collected contained a trace of fixed ammonium salt (ammonium chloride) and free hydrochloric acid, and the tar obtained amounted to about 6·5 per cent. of the weight of the coal. This tar was submitted to distillation, and the hydrocarbon $C_{10}H_{20}$ boiling between 172°—174° C. Pictet and Bouvier finishing at 300° C., when about one-half of it remained as pitch. The oils collected were carefully examined and found to contain the following substances :—

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[1] A. Pictet and M. Bouvier, *Arch. des Scien. phys. et nat. de Genève.* 1913, 1914.
[2] *Ber.*, 1915, 48, 926.
[3] Pictet and Ramseyer, *Ber.*, 1911, 44, 2486.
[4] *Brennstoff-Chem.*, 1921, 2, 312–313.
[5] *Trans. Chem. Soc.*, Vol. 105, 1914, pp. 140–151.

(*a*) A group of unsaturated hydrocarbons (ethylenic) of uncertain composition forming about 40 to 45 per cent. of the oils.
(*b*) Liquid paraffins and naphthenes, the latter being in the greater quantity, and the whole accounting for approximately 40 per cent. of the oils.
(*c*) Phenolic bodies, chiefly the cresols and xylenols, making up about 12 to 15 per cent. of the oils.
(*d*) A number of aromatic compounds, in all probability homologues of naphthalene, accounting for about 7 per cent. of the oils.
(*e*) A small quantity of solid paraffin possessing a melting-point between 52·5° and 54° C., and a molecular weight of 373·7.
(*f*) Traces of pyridine bases.

Carbon disulphide, benzene, naphthalene, and anthracene were absent ; and only a minute quantity of the homologues of benzene, such as toluene, were present.

In some further work[1] on this subject, Jones and Wheeler discovered that the liquid distillates obtained at 350° C. were the same in character as those obtained at 430° C. The yield of tar, however, was much less, being at 350° C., only 1·25 per cent. by weight of the coal, as compared with 6·5 per cent. at 430° C.

The table on next page gives a list of the chief substances which have been found, up to the present, in vacuum tars.

The low-temperature tars may be divided into two classes : (1) those obtained by the low-temperature carbonisation of bituminous coals, and (2) those produced when the lignites are submitted to low-temperature carbonisation. At this point tars of the first class only will receive consideration owing to the important part which they play in throwing light upon the subject of the formation of high-temperature tars.

In passing it should be noted that there is an essential difference between low-temperature tars from lignite and from bituminous coal, and, according to F. Fischer and W. Gluud, tars from the former are semi-solid and from the latter liquid. These workers state that liquid paraffins exist ready formed in bituminous coal and they can be extracted therefrom, while only solid products can be extracted from lignite, and these bodies appear also in its low-temperature tar. Jones[2] points out that naphthalene occurs only in tars produced above 750° C., so that its presence in a tar is a proof that the latter is not a low-temperature product.[3] In the case of genuine low-temperature tar the specific gravity of the distillate collected between 200°–300° C. is below 0·95 at 20° C., whilst in the case of other tars a fraction collected between the same points will have a specific gravity of 1·00 or higher.

The temperature at which coal should be carbonised in order to produce low-temperature tar differs according to various authorities. Fischer and Gluud[4] give

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[1] *Trans. Chem. Soc.*, Vol. 105, pp. 2562–2565. 1914.
[2] *J.S.C.I.*, 1917, 3.
[3] F. Fischer and Gluud, *Z. Angew. Chem.*, 1919, 32, 337–340.
[4] *Z. Angew. Chem.*, 1919, 32, 337–340.

550° C. as the highest temperature, whilst Bone[1] suggests 550° to 600° C., and J. D. Davis, of the U.S.A. Bureau of Mines, considers a higher temperature, viz. 750° C. as the most suitable. Another worker, S. W. Parr, places the temperature limit at 800° C. Doubtless it is necessary to vary the temperatures within the limits just quoted according to the class of coal it is desired to carbonise in order to produce a genuine low-temperature tar.

SOME OF THE CONSTITUENTS OF VACUUM TAR

Name.	Formula.	M.Pt.°C.	B.Pt.°C.	Remarks.
Ammonium Chloride .	NH_4Cl	—	—	
Hydrochloric Acid . .	HCl	—	—	
Saturated hydrocarbons—				
A solid paraffin . .	Not known	52·5–54°	—	Small quantity.
Unsaturated hydrocarbons—				
(Ethyleric) . . .	Indeterminate	—	—	A quantity.
Aromatic hydrocarbons—				
Toluene and other homologues of benzene .	$C_6H_5CH_3$	—	111°	Traces only.
Homologues of naphthalene	—	—	—	Fair quantity.
Hydroaromatic hydrocarbons—				
(Naphthenes) Hexahydromesitylene . .	C_9H_{18}	—	135°–137°	A quantity.
	$C_{10}H_{20}$	—	160°–161°	
Hexahydrodurene . .	$C_{10}H_{20}$	—	172°–174°	
	$C_{11}H_{22}$	—	189°–191°	
	$C_{12}H_{24}$	—	211°–213°	
	$C_{13}H_{26}$	—	227°–229°	
Melen	$C_{30}H_{60}$	—	218° (0·5 mm.)	
Alcoholic bodies—				
	$C_7H_{14}O$	—	—	Small quantity.
	$C_8H_{10}O$	—	—	
	$C_9H_{12}O$	—	—	
	$C_{10}H_{14}O$	—	—	
Phenolic bodies, chiefly—				
Cresols	$C_6H_4 \cdot CH_3 \cdot OH$	—	—	Fair quantity.
Xylenols . . .	$C_6H_3(CH_3)_2 \cdot OH$			
Basic compounds—				
	$C_{10}H_{11}N$ $C_{12}H_{15}N$	—	—	Fair quantity.
Pyridine bases . .	—	—	—	Traces.

At the ordinary temperature low-temperature tar is quite fluid, and its colour when examined in a thin layer varies between a golden-red and a deep wine-red. Its specific gravity is sometimes lighter and sometimes heavier than water, genuine samples testing between 0·95 and 1·06. The chief constituents of this type of tar are paraffins, olefines, naphthenes, and phenols. Aromatic hydrocarbons occur in small quantity only.

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[1] *Trans. Inst. Mech. Eng.*, No. 6, October, 1921, p. 626.

By distilling low-temperature tars with steam and discontinuing the distillation when only small quantities of oil came over, Fischer and Gluud[1] obtained distillates boiling mainly between 60° and 100° C. These distillates, after purification by treatment with alkali and acid, or with aluminium chloride, yielded perfectly coloured liquids which were unaffected by light and air. On examination they were found to contain naphthenes and paraffins, and in the case of the distillate from a tar produced from Minden coal a small quantity of benzene was found.

Further distillation of these tars yielded fractions boiling between the range 100°–125° C. and 125° and 190° C. respectively. The composition of these distillates were not definitely settled; they appear to contain paraffins, naphthenes of higher hydrogen content than those found in the fraction 60°–100° C., and certain complex aromatic compounds.

Low-temperature tars prepared by F. Fischer and W. Gluud[2] by carbonising bituminous and gas coals in a revolving furnace (which prevented the superheating of the tar and other distillation products) was found to contain naphthenes, highly viscous oils, and paraffin wax, with traces of acid and phenolic substances.

An investigation into the nature of the paraffins obtained from a low-temperature tar produced in a Mond Gas Plant fed with gas coal has been carried out by W. Gluud,[3] and this worker finds them to be chiefly a mixture of normal saturated paraffins ranging from $C_{24}H_{50}$ to $C_{29}H_{60}$. Gluud considers that the paraffins are not absolutely products of secondary processes occurring during distillation, owing to the fact that small quantities can be obtained from coal direct by extraction with benzene at 260°–270° C.

The same worker[4] obtained catechol from low-temperature tars produced from Lohberg and Saar gas coals.

According to F. Fischer, H. Schrader, and C. Zerbe,[5] low-temperature tar contains some of the derivatives of naphthalene, the chief of these being α- and β-methyl-naphthalene. The greatest amount of naphthalene derivatives occur in the fractions boiling between 240°–245° C. and 245°–250° C., obtained by distilling the tar.

W. Gluud and P. K. Breuer[6] found that low-temperature tars always contained a large but variable percentage of constituents soluble in caustic alkali solutions, the amount of these bodies being greatest in tars obtained from gas coals, reaching in some cases to 50 per cent. of the tar. These workers obtained from Lohberg

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[1] *Ber.*, 1919, 52, 1053–1068.

[2] *Ges. Abhandl. zur Kenntnis der Kohle*, 1917, 1, 114–142. *Chem. Zentr.*, 1919, 90, 11, 519–521.

[3] *Ber.*, 1919, 52, 1036–1053.

[4] W. Gluud, *Ges. Abhandl. zur Kenntnis der Kohle*, 1919, 3, 66–74. See also *Chem. Zentr.*, 1919, 90, IV, 915.

[5] *Brennstoff Chem.*, 1922, 3, 57–59. See also *Chem. Zentr.*, 1919, 90, IV, 913–915.

[6] *Ges. Abhandl. zur Kenntnis der Kohle*, 1919, 2, 236–256.

(Dinslaken) gas coals, on submission to low-temperature carbonisation, 7 to 8 per cent. of gas liquor and 10 per cent. of tar. The gas liquor contained phenolic substances amounting to 0·1 per cent. of the weight of the coal originally taken, and this amount includes a mere trace of ordinary phenol and a trace of catechol. On distilling the tar, phenols appear in the fractions boiling above 200° C.; ordinary phenol is absent, but the three cresols, the xylenols and trimethylphenols are present. The yield of cresols amounts to about 0·6 per cent. of the tar, and meta-cresol is in the largest quantity.

It should be noted that there is much less "free carbon" in low-temperature than high-temperature tars.

In the table following will be found a list of the substances which have been identified up to the present in low-temperature tars from bituminous coals.

CHIEF SUBSTANCES FOUND IN LOW-TEMPERATURE TARS FROM BITUMINOUS COALS

Name.	Formula.	Sp. Gr.	Blg. Pt. °C.	Mltg. Pt. °C.	Remarks.
Paraffins—					
$C_nH_{2n}+2$	$C_{24}H_{50}$ to $C_{29}H_{60}$	—	—	—	Also paraffin wax.
Olefines—	—	—	—	—	—
Naphthenes—	—	—	—	—	Of high hydrogen content
Phenols—					
Phenol	$C_6H_5{\cdot}OH$	1·065 @ 18°	182·6°	—	Mere trace.
o-Cresol 1 : 2	$CH_3{\cdot}C_6H_4{\cdot}OH$	1·039 @ 23°	191°	30°–31°	Meta compound occurs in largest quantity.
m-Cresol 1 : 3	$CH_3{\cdot}C_6H_4{\cdot}OH$	1·033 @ 19°	208·8°	—	
p-Cresol 1 : 4	$CH_3{\cdot}C_6H_4{\cdot}OH$	1·033 @ 23°	201·8°	35·5°	
Xylenols	$(CH_3)_2{\cdot}C_6H_3{\cdot}OH$	—	—	—	
Trimethylphenols	$(CH_3)_3{\cdot}C_6H_2{\cdot}OH$	—	—	—	
Catechol (Pyrocatechol)	$C_6H_4{<}^{OH1}_{OH2}$	—	245°	104°	
Aromatic Hydrocarbons—					
Benzene	C_6H_6	0·884 @ 15°	80·36°	5·48°	Small quantity
α-Methyl naphthalene	$C_{10}H_7{\cdot}CH_3$	1·0287 @ 12°	240°–242°	—22°	
β-Methyl naphthalene	$C_{10}H_7{\cdot}CH_3$	—	241°–242°	32·5°	

Taking into consideration what has been said upon the constitution of coal, vacuum and low-temperature tars, it appears probable that the formation of high-temperature tar, when bituminous coal is destructively distilled, is due (*a*) to the passing unchanged, through the process, of some of the constituents which occur naturally in the coal (paraffins) and which are set free during the low temperature or initial stages of the operation; (*b*) to the decomposition and also condensation, or polymerisation, of low-temperature tar constituents, these also being formed during the initial stages of carbonisation, and (*c*) to the direct decomposition of the constituents of the coal with, in many cases, subsequent polymerisations and condensations.

In the case of (*a*) it is very probable that some of the low-boiling paraffin bodies which occur in high-temperature tar get there in the manner just mentioned. It is, perhaps, advisable to study this case in conjunction with Jones and Wheeler's " bound " molecule theory,[1] as many of the substances which are considered as being original constituents of coal may be in the state suggested by these workers. Briefly, this theory assumes, for example, that the paraffins are present in coal attached chemically (or physically) to non-alkyl groups, and that some change in their state, such as can be produced by moderate heating, must take place before they can be set free. Representing the alkyl group by RH and the " bound " molecule by $RH{\cdot}C_nH_{2n}+1$, what happens when this molecule is submitted to a moderate temperature is shown by the following :—

$$RH{\cdot}C_nH_{2n}+1 \rightarrow R+C_nH_{2n}+2.$$

To illustrate case (*b*) the following examples will be useful. The naphthenes or cyclohexanes if subjected to high temperatures are converted into aromatic substances, such as benzene with elimination of hydrogen.

$$\underset{\text{cyclohexane or hexahydrobenzene}}{C_6H_{12}} = \underset{\text{Benzene.}}{C_6H_6}+3H_2$$

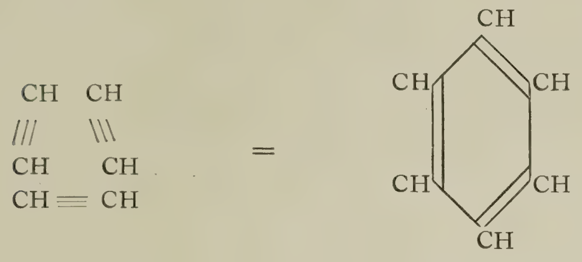
On passing hexahydrobenzene through a tube heated to 500° C., D. T. Jones[2] obtained a liquid which upon examination was found to contain approximately 20 per cent. of benzene, and also a gas which contained olefines and 26 per cent. of benzene. Zelinsky found that at 300° C. palladium black can eliminate six hydrogen atoms from cyclohexane with the formation of benzene, and although the catalytic agent used by this worker is not present under the conditions obtaining when coal tar is formed, yet another suitable catalyst (or catalysts) may be present which will assist in the splitting off of hydrogen atoms at probably a higher or lower temperature; our knowledge of catalysis and catalysts is at the moment very small, and every day new facts are being discovered in this most interesting and useful branch of physical science. It is interesting to note that when Zelinsky used the same catalyst at 100–110° C., a mixture of benzene and hydrogen was transformed into cyclohexane.

As acetylene occurs among the primary products of the destructive distillation of coal, in all probability a portion of the benzene found in coal tar is formed by the polymerisation of this hydrocarbon; and it is also probable that small quantities of both naphthalene and anthracene owe their formation to the coupling up of

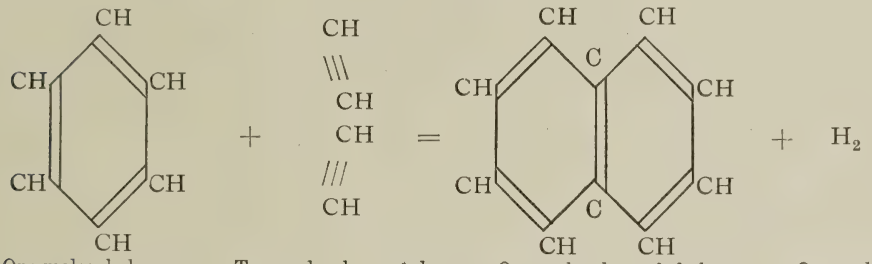
[1] *Trans. Chem. Soc.*, 1914, Vol. 105.

[2] *Trans. Chem. Soc.*, 107, 1582. 1915. *J.S.C.I.*, 36, 3. 1917.

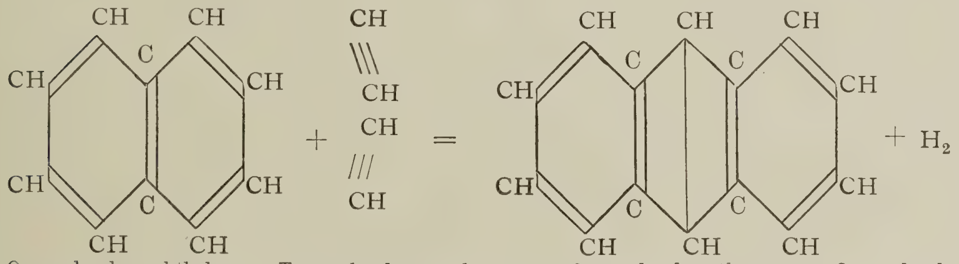
acetylene molecules with benzene or naphthalene respectively, with the elimination of hydrogen.



3 molecules acetylene. One molecule benzene.



One molecule benzene. Two molecules acetylene = One molecule naphthalene + One molecule hydrogen.



One molecule naphthalene + Two molecules acetylene = One molecule anthracene + One molecule hydrogen.

Ethylene and other olefinic bodies are found in low-temperature tars, and the work of J. E. Zanetti and M. Kandell,[1] upon the synthesis of anthracene from benzene and ethylene, points to a possible source of this aromatic hydrocarbon so far as high-temperature tar is concerned. These experimenters passed the vapours of benzene and ethylene, two parts of the former to one part of the latter, through a quartz tube heated to various temperatures in an electric furnace. They found the maximum yield was obtained at a temperature of 925° C., the amount of anthracene being 0·675 per cent. of the benzene taken. Above 925° C. there was a rapid separation of carbon and at 1000° C. anthracene was not formed.

It is very probable that the quartz tube acted more or less as a catalytic agent, and different results may have been obtained if, say, a fire clay tube had been employed. Other conditions which may affect the result are variations in pressure, speed of flow, and the presence of other gases.

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[1] *J. Ind. Eng. Chem.*, 1921, 13, 208.

The theory of Bone and Coward[1] is an important one, and concerns the case now under consideration. It is: That during the high temperatures existing in gas retorts and coke ovens while the process of coal carbonisation is going on, the primary or low-temperature distillation products of coal undergo the loss of hydrogen, and at the same time (according to the temperature obtaining) there is a loosening or dissolution of the bond between the carbon atoms. In the case of dissolution residues such as $:CH$ and $:CH_2$ are formed, and as these residues cannot exist alone, they may (1) by hydrogenisation in an atmosphere of hydrogen form methane, or (2) break down into hydrogen and carbon, or (3) form by combination with similar residues $HC:CH$ or $H_2C:CH_2$.

It is thought possible that if there is a great concentration of nascent molecules of, say, $HC:CH$ or $H_2C:CH_2$ condensations may take place with the formation of aromatic bodies.

Three examples are given below :—

Acetylene

$$\underset{\substack{\downarrow \\ \text{Polymerisation to } C_6H_6}}{CH:CH=(2(:CH))} = \left\{ \begin{array}{l} (a)\ HC:CH, \text{ or benzene.} \\ (b)\ 2C+H_2 \\ (c)\ \text{plus } 3H_2=2CH_4 \end{array} \right.$$

Ethylene

$$\underset{\substack{\downarrow \\ \text{Condensation to } C_6H_6}}{CH_2:CH_2=(2(:CH)+H_2)} = \left\{ \begin{array}{l} (a)\ C_2H_2+H_2 \\ (b)\ C_2+H_2+H_2 \\ (c)\ \text{plus } 2H_2=2CH_4 \end{array} \right.$$

Ethane

$$CH_3\cdot CH_3=(2(:CH_2)+H_2) = \left\{ \begin{array}{l} (a)\ C_2H_4+H_2 \\ (b)\ 2C+2H_2+H_2 \\ (c)\ \text{plus } H_2=2CH_4 \end{array} \right.$$

In dealing with case (*c*), as with case (*a*), some consideration must be given to the "bound" molecule theory of Jones and Wheeler. Should the assumption of these workers be correct, then the production of at least some of the paraffinoid and cyclohexane bodies found in coal tar is due to direct decomposition of the coal constituents.

At the present state of our knowledge it is very difficult to say what the chemical constitution of coal is, and what little light has been shed upon it is derived partly from deductive reasoning (*a*) from the results of vacuum and low-temperature distillations of coal, and (*b*) from investigating the substances, obtained by extracting coal with various solvents. In regard to the latter, it should be noted that before submitting coals to the action of solvents, they have, after powdering, been dried at temperatures round about 105° C., either in the ordinary atmosphere or in an inert gas, or dried *in vacuo*. During extraction the solvents are heated, and are at somewhat elevated temperatures when they come in contact with the coal. Do these conditions alter the original state of certain of the coal constituents which are dissolved out ? Possibly they do. Also there is the likelihood of some of the solvents used, say, pyridine or phenol, reacting chemically with certain bodies in the coal, changing their original form and yielding in the extract compounds dissimilar to those existing in the coal substance. However, extraction methods should not be discouraged as they, in conjunction with other methods of investigation, combined with newer and more skilful technique, will in the future, without doubt, elucidate this most difficult problem.

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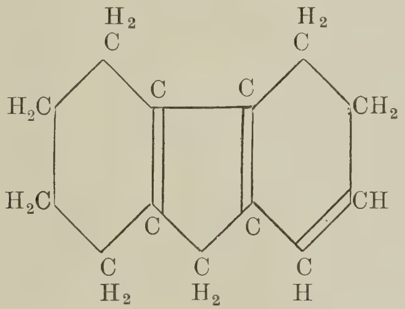
[1] *Trans. Chem. Soc.*, 93, p. 1197. 1908. *Coal and its Scientific Utilization*, 1918, p. 140.

By extracting a French coal with benzene, Pictet and Ramseyer[1] isolated a hydrocarbon possessing the following constitutional formula :—



which, when heated, yielded fluorene and hydrogen. These workers also obtained from coal, by a similar method, dihydrotoluene and dihydrometaxylene, and it is probable that a portion of the toluene, m-xylene, and fluorene found in coal tar originates from these bodies.

Jones and Wheeler,[2] by the use of pyridine on coal, and then submitting the extracted matter to the action of chloroform, obtained three groups of compounds : (*a*) those constituting the insoluble residue from the pyridine extraction of the coal ; (*b*) those constituting the insoluble residue from the treatment of the pyridine extract with chloroform, and (*c*) those constituting the portion of the pyridine extract soluble in chloroform. The (*a*) and (*b*) groups they termed "cellulosic" and the (*c*) group "resinic." When destructively distilled[3] the (*a*) and (*b*) groups yielded among other substances, phenols. The (*c*) group was found to contain alkyl, naphthene, and unsaturated hydrocarbon radicles attached to larger and more complex groupings, and this group when submitted to destructive distillation yielded chiefly paraffins, olefines, and naphthenes. It is probable that at higher temperatures than those used by Jones and Wheeler, and especially under different conditions (*e.g.* those under which high temperature tar is produced from coal), the olefines and naphthenes exist only momentarily and by condensation, and the loss of hydrogen respectively form aromatic hydrocarbons.

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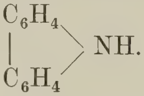
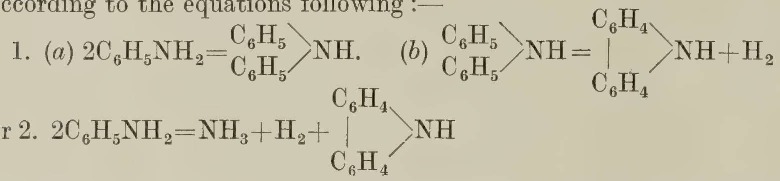
[1] *Ber.*, 1911, 44, 2486.

[2] *Trans. Chem. Soc.*, 1916, Vol. 109, pp. 707–714.

[3] *Trans. Chem. Soc.*, 1915, Vol. 107, pp. 1318–1324.

It will, no doubt, appear quite clear to the reader that the present state of our knowledge precludes making any definite statements in regard to the various reactions which take place during the formation of coal tar, and that at the moment the opinions advanced are more or less speculative. As an example take the case of carbazol  $\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right\rangle NH$. It is supposed that this substance is formed from aniline according to the equations following :—



$$1.\ (a)\ 2C_6H_5NH_2=\left.\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\right\rangle NH.\quad (b)\ \left.\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\right\rangle NH=\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right\rangle NH+H_2$$

$$\text{or }2.\ 2C_6H_5NH_2=NH_3+H_2+\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right\rangle NH$$

Now, how is the necessary aniline formed ? It is supposed that its formation comes about by the reaction of ammonia with benzene or phenol. But exactly how benzene, phenol, and ammonia originate from the constituents of coal has yet to be settled.

The continuation of careful research work in connection with the constitution of coal and the constituents of " vacuum " tar, coupled with the study of pyrogenetic reactions will, as time progresses, add much to our knowledge of the formation of the constituents of high-temperature coal tar.

A fact to be borne in mind is that the coal tars turned out by the many gasworks in the world vary very much not only in their ultimate chemical composition, but in regard to the percentage and quality of the distillates and the pitch obtained from them when submitted to distillation in a tar distillery. In practice, coal tar on distillation is split up into the following chief fractions : Ammoniacal liquor, crude naphtha, light oil, light creosote or carbolic oil, creosote, anthracene oil, and pitch, and it is from these that many valuable products are recovered.

It has been proved in practice that the nature of the raw material and the temperature of carbonisation affect the chemical composition, and, therefore, the quality of the tar. Dealing with the first condition, very shaley coal, or cannel coal, produce tars which yield on distillation products containing a large quantity of bodies of a paraffinoid nature. As paraffins are undesirable substances to certain users of coal tar distillates, the occurrence of these bodies will, of course, in such cases lower the market value. Practical working has shown that North Country coal yields a tar which on distillation gives a fairly low percentage of light oils and a rather high yield of creosote, naphthalene, and anthracene, while tar produced from Midland and Yorkshire coals yields on distillation rather more light oils and less creosote, naphthalene, and anthracene; that is, if comparative methods of carbonisation and temperatures are employed.

With reference to the effect of the temperature of carbonisation on the constitution of tars, it is found that those produced at low temperatures yield on distillation, in addition to phenols of the carbolic acid series, phenols of a different series rather less acid in behaviour, and probably of the creosol and guaiacol type. Also, there is a smaller yield of naphthalene and of the benzene hydrocarbons, and a large percentage of hydrocarbons of the paraffin and olefine series. Instead of most of the nitrogen occurring in the form of pyridine bases it appears in the form of aniline and its homologues. The amount of "free carbon" is also small. On the other hand, high-temperature tars, *i.e.* those produced at high heats of carbonisation of coal, yields on distillation only traces of paraffinoid hydrocarbons, the predominating hydrocarbons being those of the benzene, naphthalene, and anthracene series. The nitrogen occurs principally in the form of pyridine bases, and the phenols consist chiefly of carbolic acid and its homologues. The percentage of "free carbon" is generally high. In the writer's opinion the high percentage of "free carbon" is not due so much to the high heats employed as to the shape of the retort and the amount of free space. This is borne out by the comparatively low "free carbon" content of tars from heavily charged retorts, and the very low "free carbon" content of vertical retort tar. It has been found in practice that tar obtained from heavily charged retorts is of a superior quality to that produced from light charges, in that it is much thinner, contains less "free carbon" and a higher percentage of light oils. This type of tar appears to hold less water in suspension, which is a distinct advantage. Figures[1] on record show that there is a drop in the specific gravity from 1·185 to 1·105. In lightly charged retorts, in which there occurs a good deal of free space, it appears that some of the constituents of the gas and tar are "cracked," or broken up, into substances of lower molecular weight, and "free carbon," and the latter substance to a very large extent is carried up the ascension pipes and arrested by the tar in the hydraulic main. Table 9 illustrates this and gives other useful information.

TABLE 9[2]

	Tar from		
	Works using high heats and light charges. Per cent.	Works using moderate heats and fairly heavy charges. Per cent.	Continuous Vertical Retorts. Per cent.
Water . . .	2·0	2·0	2·0
Light oils . . .	1·0	6·0	5·6
Carbolic and creosote oils	14·0	32·0	41·4
Anthracene oil . .	5·0	4·0	4·0
Pitch	78·0	56·0	47·0
"Free carbon" in pitch	36	17·0	5·5

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[1] *Jour. of Gas Lighting*, October 12th, 1909.

[2] E. G. Stewart, *Trans. Lond. and Southern District Junior Gas Assn.*, 1911-1912, p. 43.

The average results of some practical distillations made by the writer, using Yorkshire, Northern, and Midland tars, are given in Tables 10, 11, 12.

TABLE 10

	Yorkshire Tar.		Northern Tar.[1]	
	Gallons per ton tar.	Per cent. by weight.	Gallons per ton tar.	Per cent. by weight.
Ammoniacal liquor .	1·8	0·82	25·10	11·5
Crude naphtha .	10·5	4·36	2·20	0·9
Light oil . .	12·3	5·43	6·70	3·0
Creosote . . .	53·5	24·84	33·60	15·6
Anthracene oil .	6·0	2·92	21·40	10·4
Pitch . . .	11·5 cwts. per ton	57·80	11·60 cwts. per ton	57·5

TABLE 11

MIDLAND TAR

	Gallons per ton tar.	Per cent. by weight.
Ammoniacal liquor . .	4·50	2·06
Crude naphtha . .	4·36	1·82
Light oil . . .	18·20	8·20
Middle oil . . .	9·20	4·26
Creosote and anthracene oil	31·80	15·10
Pitch	12·90 cwts. per ton.	64·50

TABLE 12

ULTIMATE PRODUCTS FROM MIDLAND TAR

90's benzol	1·85 gallons per ton.
90 per cent. at 160° C. . .	3·10 ,, ,,
Heavy naphtha . . .	0·75 ,, ,,
50's carbolic. . . .	3·75 ,, ,,
Cresylic	3·40 ,, ,,
Pyridine bases . . .	0·30 ,, ,,
Creosote	55·25 ,, ,,
Pitch	13·20 cwts. ,,

When considering the low-temperature tars the fact that they contain paraffinoid bodies should not be overlooked. Coalite tar is a member of the class of tars containing these bodies. This tar varies in specific gravity between 1·050 and 1·070;

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[1] A very watery type of tar.

it contains practically no "free carbon" or naphthalene, and the first products of distillation are very volatile. It is these distillates which contain the paraffin bodies, and from the tar distiller's point of view the value of the tar is much reduced by this fact. It should find use as a fuel oil, or if sufficient volume can be obtained to warrant separate storage and distillation, the lighter distillates could be employed, after rectification, for motor spirit and the heavier distillates for fuel oil. Table 13 gives the results of two analyses of coalite tar.

TABLE 13

COALITE TAR

(a)[1]		(b)[2]	
Specific gravity	1·07	Specific gravity	1·075
	Per cent.		Per cent. by vol.
Below 170° C.	10·8	Water	2·64
170°–270° C.	20·0	Up to 170° C.	3·10
270°–350° C.	30·0	170°–225° C.	13·72
Pitch	39·2	225°–240° C.	8·35
		240°–270° C.	8·35
		270°–300° C.	8·80
		300°–320° C.	12·31
			Per cent. of Tar.
		Pitch	40·00

On examination a sample of coalite pitch gave 85·1 per cent. of volatile matter by the method given on page 388, 99·6 per cent. of combustible matter, and 0·35 per cent. of ash.

Unfortunately, vertical retort tar exhibits the same fault as coalite tar in that it contains paraffinoid bodies. On this account it is not possible to prepare from it suitable benzole and toluole from which to manufacture pure benzene and toluene and their derivatives. From an inspection of Table 14 it will be seen that the specific gravity of this tar and also the "free carbon" content are very low. On distillation, compared with coal tar from horizontal or inclined retorts, it yields a smaller percentage of benzole and toluole, very little phenol, and practically no naphthalene. The pitch is of a finer quality than that obtained from horizontal or inclined retort tar, in that it is brighter and contains very little "free carbon."

TABLE 14

VERTICAL RETORT TAR (DESSAU)

			Per cent. by weight.
Specific gravity	1·084	Ammoniacal liquor	4·40
	Per cent.		
"Free carbon"	1·06	Up to 170° C.	3·75
Volatile in pitch	77·7	170°–270° C.	33·60
——		270°–350° C.	8·00
Specific gravity of pitch	1·19	Pitch	48·25

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[1] *Gas World*, May 5th, 1909, p. 654.

[2] Prof. Lewes (see *Chem. Trade Jour.*, December 23rd, 1911, p. 633).

TABLE 15

VERTICAL RETORT TAR (GLOVER-WEST CONTINUOUS)[1]

Specific gravity	1·074
	Per cent.
" Free carbon "	3·40
Pitch	very soft

	Per cent. by weight.
Water	1·3
Light oils to 170° C.	5·0
Carbolic oils to 230° C.	16·0
Creosote oils to 270° C.	8·9
Anthracene to 310° C.	7·9
Pitch	60·9

J. Dickson[2] gives the following results of the working up of 163,370 gallons of vertical retort tar.

TABLE 16

Sp. gr. of tar	1·080
	Per cent.
Water	= 6·77
Oil to 170° C.	= 9·28
170° to 270° C.	= 23·02
270° to 315° C.	= 9·86
Pitch	= 51·07
	100·00

		Galls.
Crude naphtha, sp. gr.	0·930 =	12,249
Light creosote ,,	1·020 =	36,089
Prepared tar ,,	1·160 =	103,880
Liquor 5 oz. strength	=	8,900
Distillation loss	=	2,252
		163,370

Pitch contained 5·23 per cent. of " free carbon."

The following table, by the late Mr. J. West, gives the average amount of benzene, toluene, and paraffin bodies yielded from vertical retort tar as compared with horizontal retort tar.

TABLE 17

	Vertical Retort Tar.	Horizontal Retort Tar.
Benzene	0·7 per cent.	1·4 per cent.
Toluene	0·3 ,,	0·5 ,,
Paraffins	0·3 ,,	Traces.

In Tables 18, 19, and 20, by G. H. Sharples,[3] some interesting comparisons are made between vertical and horizontal retort tars.

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[1] D. Fulton, *Gas World*, March 13th, 1915, p. 298.

[2] *Gas World*, October 26th, 1918, p. 251.

[3] *Gas World*, September 8th, 1917, pp. 159–160.

TABLE 18

ANALYSIS OF TARS FROM SAME CLASS OF COAL

	Horizontal Retorts. Per cent.		Vertical Retorts. Per cent.	
Water	1·55		2·42	
Crude naphtha	2·62	12·06	2·44	18·55
Light oils	9·44		16·11	
Carbolic oil	12·09		14·10	
Creosote oil	13·00		21·47	
Pitch	61·30		43·38	
Loss	—		0·08	
	100·00		100·00	
Specific gravity of tar at 60	1·20		1·075	

TABLE 19

ULTIMATE ANALYSIS OF TARS FROM SAME CLASS OF COAL

	Vertical Retorts.			Horizontal Retorts.		
	Gals. per ton.	Per cent. by weight.	Pounds ton coal carbonized.	Gals. per ton.	Per cent. by weight.	Pounds ton coal carbonized.
90's benzole	1·340	0·515	0·747	2·507	0·984	1·299
90's toluole	0·832	0·317	0·460	0·818	0·318	0·420
Solvent naphtha	4·252	1·615	2·342	2·537	0·986	1·302
Total naphtha	6·424	2·447	3·549	5·862	2·288	3·021
Heavy naphtha	6·240	2·409	3·493	3·979	1·652	2·178
Refined pyridine	0·354	0·160	0·232	0·160	0·76	0·100
Heavy pyridine bases	0·832	0·383	0·555	1·165	0·532	0·702
60's carbonic acid	2·311	1·074	0·557	0·200	0·094	0·124
Cresylic acid	12·48	5·913	8·574	5·230	2·451	3·234
Light creosote	16·039	7·126	10·339	43·065	20·381	26·902
Heavy creosote	66·102	31·009	44·965			
Naphthalene	6·839	3·455	5·017	9·00	4·620	6·098
Pitch	—	43·380	62·901	—	66·425	87·7
Amm. Liq. 3·3 per cent. NH_3	5·366	2·420	2·030	2·980	1·356	1·800
Loss	0·322	0·224	0·325	0·280	0·125	0·165

TABLE 20

Amount of Paraffins in Light Distillates from Vertical and Horizontal Retort Tars

	From Vertical Retorts.		From Horizontal Retorts.	
	Paraffin.	Sp. Gr.	Paraffin.	Sp. Gr.
	Per Cent.		Per Cent.	
90's benzole .	19	0·865	Below 1	0·881
90's toluole .	12	0·863		0·872
Solvent . .	6	0·851		0·871

A very interesting set of figures dealing, so far as the tar is concerned, with the effect of passing steam into vertical retorts during carbonisation will be found in Table 21. These figures have been taken from the Fourth Report of the Research Sub-Committee of the Gas Investigation Committee, the tests being carried out at the Uddingston Gasworks.[1]

TABLE 21

Analyses of Coal

	1	2	3	4	5
Proximate analysis :—					
Moisture	9·8	10·9	10·1	10·5	10·3
Volatile matter . . .	32·7	32·4	32·5	32·6	33·1
Fixed carbon	50·5	49·9	48·9	49·9	50·0
Ash	7·0	6·8	8·5	7·0	6·6
Ultimate analysis of dry coal :—					
Ash	7·0	6·8	8·5	7·0	6·6
Carbon	74·5	75·3	74·1	74·6	74·2
Hydrogen	5·6	5·6	6·0	5·4	5·6
Sulphur	1·3	1·1	1·1	1·1	1·2
Nitrogen	1·9	1·9	1·9	2·1	2·0
Oxygen	9·7	9·3	8·4	9·8	10·4

Details in regard to Temperatures and Steam used

Average temperature of circulating flues	1115°	978°	1129°	1128°	1096° C.
Average temperature of combustion flues	1211°	1139°	1177°	1186°	1090° C.
Steam passed into retorts :—					
Diameter, approximate, of nozzles	No steam	$\frac{5}{16}$ in.	$\frac{5}{16}$ in.	$\frac{5}{16}$ in.	$\frac{5}{16}$ in.
Pressure on nozzles in lbs. per sq. in.	—	Normal	5·16	10·02	15·20

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[1] *Gas World*, June 5th, 1920, pp. 492–504.

Steam delivered per nozzle in lbs.	1	2	3	4	5
per minute	—	0·681	1·275	1·75	2·16
Total steam used in tons	—	28·0	45·9	63·2	100·1
Steam per cent. on coal used	—	13·3	22·1	32·7	44·8
Tar (dry) in gallons per ton of coal	13·2	16·4	16·8	20·4	21·2

ANALYSES OF TAR

Sp. gr. @ 60 Fahr.	1·083	1·083	1·082	1·081	1·082
Per cent. by volume :—					
Liquor	2·62	3·41	4·71	5·40	5·33
50/90 benzole	0·34	0·31	0·31	0·26	0·23
90/160 naphtha	0·81	0·93	0·87	0·88	0·65
90/190 naphtha	1·65	1·46	1·34	1·64	1·49
60 F. carbolic	0·24	0·24	0·23	0·24	0·25
Creosote and Anthracene, including tar acids	48·27	44·10	40·87	38·63	38·22
Benzene with paraffin	0·30	0·29	0·30	0·24	0·15
Benzene (corrected)	0·24	0·24	0·24	0·20	0·12
Toluene with paraffin	0·30	0·25	0·25	0·29	0·24
Toluene (corrected)	0·27	0·23	0·23	0·27	0·22
Per cent. by weight :—					
Pitch (med. soft)	48·50	49·80	52·80	53·60	56·90
"Free carbon" in tar	1·50	1·30	1·10	0·70	0·40

The results of some tests made by the late Mr. J. West on tar obtained from Haigh Moor Coal will be found in Table 22.[1] These figures are of interest, as they show the effect of high and medium temperatures upon the tar when the coal is carbonised in vertical retorts, and also the type of tar obtained when using horizontal retorts. While these tests were being carried out, Dr. F. M. Perkin suggested passing stripped gas through the retorts with the idea of increasing the volume of tar and other liquid products. The proposal was carried out, and it was found that the tar yield increased by two to three gallons per ton of coal.

TABLE 22

ANALYSIS OF COAL

Moisture	2·29 per cent.
Volatile matter	31·64 ,,
Ash	6·37 ,,

Test carried out in horizontal test plant.

Time of carbonising	4 hours.	
Temperature of carbonisation.		
Outside retorts	1373° C.	Average.
Inside retorts	1048° C.	

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[1] J. West, *Gas World*, November, 1917, p. 242.

Test of dehydrated tar.

0° to 170° C.	10 per cent.
170° to 230° C.	15 ,,
230° to 360° C.	21 ,,
Pitch and loss	54 ,,

Test carried out in vertical retorts (Glover-West).

	High Tempr.	Medium Tempr.
Temperature outside retorts	1362° C.	1160·0
Tar per ton of coal, dehydrated	16·06 galls.	16·5 galls.
Am. sulphate per ton of coal	23·60 lbs.	26·00 lbs.
Analysis of tars.		
Specific gravity	1·143	1·072
0° to 170° C.	3·14 per cent.	4·6 per cent.
170° to 230° C.	19·67 ,,	21·1 ,,
230° to 360° C.	32·97 ,,	31·4 ,,
Pitch and loss	44·22 ,,	42·9 ,,

The effect of steaming on vertical retort tar is admirably shown in Table 23.[1]

TABLE 23

COAL USED: ORRELL NUTS

	High temps. Five days' experiments.	High temps. Two days' steaming to make Blue Water Gas. 25 lb. pressure through $\frac{1}{8}$-inch Nozzle.	High temps. Two days' steaming to make Blue Water Gas. 40 lb. pressure. $\frac{1}{8}$-inch Nozzle.	High temps. Two days' steaming to make Blue Water Gas. 45 lb. pressure. $\frac{1}{8}$-inch. Nozzle.
Temperature outside retorts (average)	1393° C.	1397° C.	1387° C.	1415° C.
Tar per ton dehydrated	16·8 galls.	17·7 galls.	20·0 galls.	17·8 galls.
Am. liquor, 10 oz. per ton	33·3 ,,	32·6 ,,	43·9 ,,	—
Specific gravity	—	1·0905	1·0146	1·0665
0° to 170° C.	1·50 per cent.	2·5 per cent.	1·5 per cent.	2·0 per cent.
170° to 230° C.	15·75 ,,	13·5 ,,	13·5 ,,	10·0 ,,
230° to 360° C.	36·00 ,,	37·0 ,,	39·5 ,,	44·0 ,,
Residue	46·75 ,,	47·0 ,,	45·5 ,,	44·0 ,,

In Table 24 are given some very interesting figures showing the effect of continuous steaming of coal during distillation in Glover-West vertical retorts. The experiments were carried out by J. E. Blundell.[2]

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[1] J. West, *Gas World*, November 10th, 1917, p. 343.

[2] *Gas World*, November 3rd, 1917, pp. 322–326.

TABLE 24

With Steaming

	Per ton coal.
Ammoniacal liquor, 10 oz.	32·68 galls.
Tar	16·61 ,,
Specific gravity of tar	1·08

Crude Products.	Gallons per ton of tar.	Per cent. by weight.
Ammoniacal liquor at 2·17 per cent. NH_3	12·69	5·66
Crude benzole, sp. gr. ·873	11·23	4·38
Middle oil, sp. gr. ·980 (up to 270° C.)	60·00	26·25
Heavy creosotes, sp. gr. 1·047	45·50	21·26
Pitch, medium soft		41·00
Loss		1·45
		100·00

Products after further Treatment.		
90's benzole	1·80	0·71
90's toluole	0·95	0·37
Solvent naphtha	4·04	1·57
Tar acids	20·65	9·68
Crude pyridine	2·36	1·09
Total creosote	84·18	37·58
Pitch		41·00
Ammonia water and loss		8·00
		100·00

The tar contained 4·58 per cent. of "free carbon."

Without Steaming

	Per ton coal.
Ammoniacal liquor, 10 oz.	25·3 galls.
Tar	10·59 ,,
Specific gravity of tar	1·087

Crude Products.	Gallons per ton of tar.	Per cent. by weight.
Ammoniacal liquor at 2·6 per cent. NH_3	9·21	4·11
Crude benzole, sp. gr. ·860	7·30	2·80
Middle oil, sp. gr. ·968 (to 270° C.)	57·86	25·00
Heavy creosote, sp. gr. 1·03	40·92	18·82
Pitch, medium soft		47·7
Loss		1·52
		100·00

Products after further Treatment.

	Gallons per cent. of tar.	Per cent. by weight.
90's benzole	1·17	0·46
90's toluole	0·50	0·19
Solvent naphtha	2·81	1·09
Tar acids	18·87	8·84
Crude pyridine	2·70	1·25
Total creosote	77·10	33·92
Pitch		47·75
Ammonia water and loss		6·50
		100·00

The tar contained 5·20 per cent. of "free carbon."

Some important figures are given in Table 25 relative to a vertical retort tar obtained from Kent coal. They were obtained by the late Mr. J. West.[1]

TABLE 25

Test Plant, Glover-West Vertical : 4 Retorts

Coal used : Kent coal ex-Beresford seam

Analysis of Coal

Moisture	1·95 per cent.
Volatile matter	19·12 ,,
Ash	11·21 ,,

	High temp.	Low temp.
Duration of test	4 days	4 days
Temperature taken outside retort	1400° C.	978° C.
Tar per ton of coal (dehydrated)	6 galls.	10·89 galls.
Am. sulphate per ton coal	11·6 lbs.	26·2 lbs.

Analysis of Tars

	High temp.		Low temp.
Specific gravity @ 60° Fahr.	1·051		1·036
0° to 168° C.	2·90 per cent.	0° to 160° C.	5·00 per cent.
168° to 228° C.	11·60 ,,	160° to 240° C.	16·50 ,,
288° to 268° C.	7·90 ,,	240° to 360° C.	27·00 ,,
Pitch	—		51·50 ,,
Benzole in tar	1·53 ,,		1·68 ,,
Toluole in tar	0·59 ,,		0·34 ,,

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[1] J. West, *Gas World*, November, 1917, p. 341.

In Table 26 is given the analysis of a tar obtained from Dessau vertical retorts, and this is compared with a horizontal retort tar.

TABLE 26

	Dessau Vertical Retort Tar.	Horizontal Retort Tar.
Specific gravity @ 15·5° C.	1·113	1·220
"Free carbon"	4·0 per cent.	17·25 per cent.
Tar Acids	5·3 ,,	3·0 ,,
Distillate :—		
Up to 170° C.	13·0 ,,	4·9 ,,
170° to 270° C.	24·0 ,,	18·4 ,,
270° to 350° C.	9·0 ,,	9·0 ,,
Pitch	50·0 ,,	60·6 ,,

In Table 27 will be found some figures relating to tar obtained from Woodall-Duckham vertical retorts.

TABLE 27

DISTILLATION OF TAR OBTAINED FROM WOODALL-DUCKHAM VERTICAL RETORTS [1]

	No. 1. Moderate heats. Per cent.	No. 2. Higher heats. Per cent.
Up to 100° C.	1·5	0·6
100°–130° C.	1·0	1·8
130°–170° C.	2·2	0·4
170°–230° C.	11·4	16·2
230°–270° C.	17·5	14·2
270°–330° C.	18·0	15·7
330°–350° C.	12·4	6·9
350°–370° C.	12·0	9·0
Pitch	24·0	35·2

The writer considers the figures given by Tooby for the pitch are rather too low. On the practical scale distillation is stopped at a temperature varying between 310° and 320° C., whereas in the table the residue above 370° C. has been taken as pitch.

Tars obtained from coke ovens are usually viscid and sometimes more or less sticky, and they vary in specific gravity from about 1·100 to 1·200. The yield of coke oven tar per ton of coal averages out at about 9 gallons, and the distillates obtained from this kind of tar contain far more paraffin bodies than those from horizontal or inclined retort tars; in fact, coke oven tar can be considered as a paraffinoid tar. The amount of paraffins in this tar is increased if the ovens are fully charged with uncrushed small coal, and if this type of coal is used and it is desired to keep the paraffin content of the tar low, then it is necessary to lightly charge the ovens, allowing some free space above the charge, and to keep outside temperature the same as before.[1] In by-product coking it is usually the practice to employ crushed coal, fully charge the ovens and work at high temperatures; between 1200° and 1400° C. outside the ovens. This procedure keeps the paraffin content of the tar on the low side.

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[1] Chas. F. Tooby, "Notes on the Working of the Woodall-Duckham Installation of Vertical Retorts at Windsor Street, Birmingham." M. J. G. Assn., *Gas World*, January 24th, 1914.

In Tables 28, 29, 30, 31 will be found the analyses of four coke oven tars.

TABLE 28[2]

COKE OVEN TAR

Light oils up to 170° C.	24·9 per cent.
Creosote oils	25·9 ,,
Heavy oil	9·3 ,,
Above 270° C.	11·4 ,,
Pitch (per cent. of total tar)	28·0 ,,
" Free carbon " in tar	3·5 ,,

TABLE 29

KLÖNNE CHAMBER OVEN TAR

Specific gravity @ 68° Fahr.	1·1359
Ammoniacal liquor	2·0 per cent.
" Free carbon "	3·3 ,,
Tar acids	6·1 ,,
Napthalene	7·6 ,,
Pitch of good quality	54·0 ,,

TABLE 30[3]

SEMET-SOLVAY COKE OVEN TAR

Specific gravity	1·170
Light oil, 80°–170° C.	3·7 per cent.
Middle oil, 170°–230° C.	9·8 ,,
Creosote oil, 230°–270° C.	12·0 ,,
Anthracene oil, over 270° C.	4·3 ,,
Pitch	67·0 ,,
Water	2·3 ,,

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[1] A. H. Middleton, "Construction of Coke Ovens," Paper read before the Coke Oven Managers' Association, December 20th, 1919.

[2] W. Chaney, *Gas World*, June 21st, 1913.

[3] V. B. Lewes, *The Carbonisation of Coal*, 1912, p. 205.

TABLE 31[1]

DISTILLATION OF COKE OVEN TAR (DRY SAMPLE)

170° C.	0·65 per cent.
170° to 230° C.	0·15 ,,
230° to 270° C.	3·86 ,,
270° to 300° C.	5·60 ,,
300° C.	21·65 ,,
Pitch, softening point 59° C.	68·09 ,,

Blast furnace tar is recovered from the gases which leave those blast furnaces fed with coal, generally of the type known as splint coal. The nature of this tar is somewhat different to that of the tars obtained when coal is carbonised for gas production; its specific gravity is lower and it is sometimes lighter than water [approx. 1·010—0·960], contains little or no naphthalene, benzene and anthracene are practically absent, but toluene and the xylenes, chiefly meta-xylene, are present, and it contains a large quantity of phenolic bodies, many of which are not of the same series as carbolic acid. Among these bodies are found phenol in very small quantity, a larger amount of the cresols, and greater quantities of meta-xylenol, pseudocumenol and the naphthols, and in all probability phenols of the guaiacol and creosol type. It is to the presence of these higher boiling and less corrosive phenolic bodies that blast-furnace creosote owes its value as a raw material in the manufacture of high coefficient disinfectants. The paraffin content of blast furnace tar is high. Table 32, due to Watson Smith, gives the analysis of a blast-furnace tar.

TABLE 32.

		Volume.	Weight.	Sp. Gr.
Specific gravity of the tar	0·954			
Distillate below 230° C.	Water	30·60	32·3	1·007
	Oil	2·91	2·8	0·899
230°–300° C.		6·97	7·1	0·971
300° C. until oils solidify		13·02	13·5	0·994
Paraffin scale		16·75	17·3	—
Coke		—	21·5	—
Loss		—	5·5	—

Water-gas tar fresh from the water-gas plant contains a considerable quantity of water, which is held in a more or less emulsified state. The amount may be below 40 per cent. or much above 60 per cent. This water is usually separated by centrifugalising the heated tar, and a dehydrated tar is often obtained by this means which contains about 1 per cent. Water-gas tar is a more or less fluid material of an oily nature, and its specific gravity varies between about 1·010 and 1·140; naturally the amount of emulsified water present will affect the specific gravity. In colour this tar is brownish black, and its content of "free carbon" is generally very low, often not more than a trace. Paraffin bodies may or may not occur in water-gas tar; tar from a plant which is working properly is free from these bodies. It is notable that pyridine and other basic substances, and also phenols, are absent from this tar. The benzenoid hydrocarbons and also naphthalene and anthracene occur in varying quantities, and the high-boiling substances which go to form pitch are present in a much smaller quantity than in coal tar. In Tables 33, 34, 35, 36, 37, will be found the analyses of various samples of water-gas tar.

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[1] J. Curry, *Gas World*, April 1st, 1922, p. 14 (Coking Section).

TABLE 33[1]

Water	6·5 per cent.
Light oils distilling up to 170° C. .	6·5 ,,
Middle oils ,, ,, 230° C. .	9·0 ,,
Heavy oils ,, ,, 270° C. .	18·5 ,,
Anthracene oils	42·0 ,,
Specific gravity	1·086 ,,

TABLE 34[2]

Water-gas tar obtained from water gas carburetted with Russian crude oil.

Benzole . . .	1·19 per cent.
Toluole . . .	3·83 ,,
Light paraffin . .	8·51 ,,
Solvent naphtha . .	17·96 ,,
Phenol	traces.
Middle oil . . .	29·44 ,,
Creosote oil . . .	24·26 ,,
Naphthalene . . .	1·28 ,,
Anthracene . . .	0·93 ,,
Coke	9·80 ,,

TABLE 35[3]

WATER-TAR GAS

Specific gravity of the tar	1·100	
	Per cent.	
80° to 200° C. . .	9·2 {$\frac{1}{3}$ oil. $\frac{2}{3}$ water.	
200° to 270° C. . .	11·2 solids. 17·7 oil.	Chiefly naphthalene; 0·82 per cent. anthracene.
270° to the formation of pitch . . .	6·0 solids. 26·5 oil.	25·6 per cent. anthracene. 3·0 per cent. anthracene.
Continued distillation .	1·7 semi-solid. 6·0 oil.	2·0 per cent. anthracene.

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[1] Zwarg, *Jour. f. Gasbel.*, 1911, p. 837.

[2] Mathews and Goulden, *Gas World*, 16, p. 625. *Fischers Jahresber.*, 1892, p. 77.

[3] A. H. Elliott, *Amer. Chem. Jour.*, 1884, p. 248.

TABLE 36[1]

WATER-GAS TARS

Sample.	1.	2.	3.	4.
Water	1·5	1·0	—	—
Light oil	3·5	6·5	—	1·39
Middle oil	30·5	9·0	5·80	15·45
Heavy oil	20·0	18·5	9·16	—
Anthracene oil	25·5	42·0	34·34	42·39
Pitch	19·0	23·0	39·91	18·23

TABLE 37[2]

WATER-GAS TARS

Specific gravity at 15° C.	1·13°
" Free carbon "	0·60 per cent.
Tar bodies (bitumen, pitch)	51·0 ,,
Tar acids	none.
Solid napthalene	,,
Distillate below 170° C.	0·50 per cent.
,, from 170° to 205° C.	0·50 ,,
,, ,, 205° to 235° C.	1·70 ,,
,, ,, 235° to 255° C.	4·10 ,,
,, ,, 255° to 270° C.	5·80 ,,
,, ,, 270° to 315° C.	15·00 ,,
Residue above 315° C.	72·40 ,,

The particulars given in Table 38[3] relating to a cannel coal tar will no doubt be of interest.

TABLE 38

TAR FROM HINDLEY CANNEL

Tar yield per ton of cannel	8 gallons.
Specific gravity @ 20° C.	1·149.
Distillation :	
Up to 170° C.	6·8 per cent.
170° to 230° C.	15·5 ,,
230° to 270° C.	8·95 ,,
270° to 330° C.	22·9 ,,
Pitch (brittle)	45·0 ,,

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[1] L. Schmitz, *Die Flussugen Brennstoffe*, 1912.

[2] Forest, *United-Otto-Ofen.*

[3] F. S. Sinnatt and M. Barash, Bull. 6, *Lancs. and Cheshire Coal Research Assn.*, 1920, 15.

It appears that the yield of naphthalene is much smaller and the yield of anthracene much larger from cannel tar than from coal tar.

The constitution of low-temperature tar obtained from bituminous coal has already received attention [pp. 62–67]. However, the following further particulars and tables dealing with this class of tar, (a) obtained from lignites and (b) from true coals will, without doubt, prove useful for purposes of comparison.

In Table 39[1] will be found the analysis of a low-temperature tar obtained by carbonising coal (bituminous) at a low temperature in rotary retorts. The yield of tar per ton of coal carbonised amounted to 20 gallons, and the quantity of cresols recovered averaged 20 per cent., while the amount of "free carbon" in the pitch obtained by distilling the tar varied between 0 and 4·5 per cent.

TABLE 39

Light oils up to 180° C. . .	4·75	per cent.
Medium oils from 180°–230° C. .	20·00	,,
Heavy medium oils from 230°–270° C.	14·50	,,
Heavy oils from 270°–320° C. .	24·00	,,
Pitch	35·00	,,
Loss	1·75	,,

F. Fischer and W. Gluud[2] by using a revolving furnace avoid the super-heating of products of distillation and obtained considerable quantities of low-temperature tars which are characterised by the presence of naphthenes, highly viscous oils and paraffin wax, and by the absence of aromatic compounds. Gas coal and cannel coal yield 10 per cent. and 14 per cent. of tar by weight respectively, whilst gas coals in tar recovery producer systems yield 15 per cent. of tar. The following table [No. 40] is given as a contribution to the knowledge of the properties of these tars.

TABLE 40

	Tar from low temperature distillations.		Tar from producer systems.
	Bituminous coal. %	Gas coal. %	Gas coal. %
Non-viscous oils . .	33·5	15·0	17·7
Viscous oils (lubricants) .	15·2	10·0	11·3
Phenols	14·0	50·0	37·8
Solid paraffin . . .	00·4	1·0	0·8
Resins	4·2	1·0	0·7
Pitch	19·2	6·0	15·0
Loss and water . .	13·5	17·0	16·7

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[1] Harold Nielsen, *Gas World*, November 12th, 1921, p. 433.

[2] *Ges. Abhandl. zur Kenntnis der Kohle*, 1917, 1, 114. See also Applied Chemistry Report [*S.C.I.*], Vol. 4, p. 57.

It would appear that the tar derived from complete gasification systems possess many of the characteristics attributed to low-temperature tar.

W. Schneider[1] examined two low-temperature tars, one obtained from a non-bituminous Rhenish lignite containing 15 per cent. of moisture and 3–4 per cent. of bitumen, and a Central German lignite containing 20–30 per cent. of moisture and 15–16 per cent. of bitumen. The tars were prepared by distilling the lignites with superheated steam, the maximum temperature being 450° C., and a Fischer and Gluud apparatus was used. The tars differed in consistence from low-temperature tars obtained from pit coal (bituminous coal), their setting points were 33° C. and 37° C., and their specific gravities at 50° C., 0·995, and 0·883–0·890. On submitting these tars to fractional distillation in superheated steam the following results were obtained.

TABLE 41

	Bituminous lignite.	Non-bituminous lignite.
Low-temperature tar from 100 kilos of lignite (dry substance)	24 kilos of tar (16 per cent. creosote)	7·6 kilos of tar (36–38 per cent. creosote)
Viscous oils (freed from phenols)	17·2 per cent.	14·8 per cent.
Viscosity at 20° C., °Engler .	13·5°	18·0°
,, ,, 50° C. ,, .	2·9°	3·6°
Comprising fractions :—		
(*a*) Of high viscosity .	1·73 per cent. (V^{20}=67° E.)	2·8 per cent. (V^{92}=7·4° E.)
(*b*) Of medium ,, .	13·01 per cent. (V^{20}=11·4° E.)	8·9 per cent. (V^{20}=8·5° E.)
(*c*) Of low ,, .	2·47 per cent. (V^{20}=5·4° E.)	3·1 per cent. (V^{20}=7·5° E.)
Hard and soft paraffins (montan wax, etc.) . . .	29·4 per cent.	13·0 per cent.
Non-viscous oils . . .	28·9 ,,	26·2 ,,
Acid fraction . . .	10·5 ,,	24·7 ,,
Resin	2·2 ,,	2·3 ,,
Pitch	3·2 ,,	8·5 ,,

At the moment lignite tar is not a commercial commodity, at least in Great Britain, but the analysis given in Table 42 is of interest to compare with tars obtained from bituminous coals.

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[1] *Ges. Abhandl. zur Kenntnis der Kohle*, 1919, 2, 80–127. *Chem. Zentr.*, 1919, 90, IV, 935–937.

TABLE 42[1]

LIGNITE TAR

Proximate Analysis of Lignite :—	
Fixed carbon	15·17
Volatile matters	36·95
Sulphur	1·17
Ash	26·15
Water	20·56
	100·00
Yield of tar, gal. per ton lignite	4·5
Specific gravity of tar	1·18
Analysis of Tar :—	
Light oils (at 170° C.)	4·4
Middle oils (between 170° and 270° C.)	13·6
Heavy oils (between 270° and 300° C.)	6·8
Pitch	75·2
	100·0
Benzole and toluole	0·3
Tar acids	2·2
Naphthalene	1·8
Yield of liquor, gal. per ton lignite	35·2
Analysis of liquor :—	Per cent.
Ammonia	0·41

In Table 43 is given the analysis of a tar obtained from a complete gasification plant, the results of some very useful work by Frank H. Robinson.[2] This investigator states that " Owing to the lower temperature in the retorts, a thin tar is obtained which has had no time to be " cracked " because of the water gas sweeping the gas forward to the ascension pipes as quickly as it is produced."

TABLE 43

The coal carbonized was a mixture of Yorkshire and Durham, an average sample as charged into the retorts giving the following analysis :—

	Per cent.	
Moisture	2·87	
Volatile matter	29·50	Dry basis.
Fixed carbon	57·00	
Ash	13·50	

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[1] *Gas World*, August 14th, 1920, p. 122.

[2] *Gas World*, May 7th, 1921, p. 369.

	From complete gasification plant.	From horizontal retorts.
Specific gravity	1·12	1·20
Water	5·2 per cent.	3·5 per cent.
Light oils to 170° C.	1·6 ,,	1·3 ,,
Oil, 170°—230°	3·4 ,,	5·2* ,,
,, 230°—270°	13·8 ,,	16·3* ,,
,, 270°—300°	7·2 ,,	5·1* ,,
Residue (pitch)	68·8 ,,	68·6 ,,
	100·0 ,,	100·0 ,,

No naphthalene separated from oils on standing overnight.

*Fractions 170° to 270° rich in naphthalene, and became semi-solid on cooling. Fraction 270° to 300° deposited considerable crop of crystals.

In Table 44 details of the analyses of tars obtained in the production of Carbocoal are set out, and for comparison the analysis of a coke oven tar is given. For particulars of Charles H. Smith's Carbocoal process the reader is referred to the journals mentioned in the footnotes 1, 2, 3, 4.

TABLE 44

	Distillation temperature.	By-product coke oven.		Carbocoal, first distillation.		Carbocoal, second distillation.	
	Cent.	Gal.	Per cent.	Gal.	Per cent.	Gal.	Per cent.
Light oil	0–170	0·27	3·47	1·58	6·60	0·003	0·05
Middle oil	170–230	0·44	5·85	3·29	13·70	0·036	0·60
Creosote oil	230–270	0·78	10·37	3·11	12·95	0·126	2·10
Heavy oil	270–360	1·26	16·81	8·88	37·00	2·485	41·42
Pitch	—	4·66	62·18	6·90	28·75	3·290	54·83
Loss	—	0·09	1·32	0·24	1·00	0·060	1·00
Totals		7·50	100·00	24·00	100·00	6·000	100·00

In Table 45 will be found an analysis of a tar obtained from an American coal when carbonised in the "Glasgow" continuous-intermittent vertical retorts.[5] The low amount of soft pitch should be noted.

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[1] *Gas World*, October 5th, 1918, Coking Section, p. 17.

[2] *J.S.C.I.*, 1920, 308R. *J.S.C.I.*, 1918, 697A. *J.S.C.I.*, 1921, 51T.

[3] *Gas J.*, 1919, 147, 504.

[4] W. Savage, *Chem. and Met. Eng.*, 1918, 19, 597.

[5] *Gas World*, November 19th, 1921, pp. 446–447.

TABLE 45

Analysis of Coal Used

	As fired.	Dry.
Fixed carbon . .	58·89	59·81
Volatile matter . .	30·94	31·43
Ash	7·78	7·90
Sulphur . . .	·85	·86
Moisture . . .	1·54	Nil.
	100·00	100·00
Nitrogen . . .	1·52	1·54

Analysis of Tar Obtained

Sp. Gr.	1·0609
"Free carbon" content	2·090 per cent. (by weight)

	By weight.	By volume.
1st distillate up to 170° C. (338° Fahr.)—		
Water	12·0	11·2
1st light oils	6·9	5·1
2nd distillate up to 230° C. (446° Fahr.)—		
2nd light oils	16·2	15·6
3rd distillate up to 270° C. (518° Fahr.)—		
Creosote oils	8·2	7·6
4th distillate up to 310° C. (590° Fahr.)—		
Anthracene oils	10·9	9·9
5th distillate—		
Oils above 310° C. . . .	12·3	11·1
Pitch (soft)	32·7	
Loss	·8	
Total	100·0	

In a paper read before the Scottish Junior Gas Association, Dr. Davidson[1] gave some interesting figures dealing with the variation in the composition of tar according to the kind of retort and the carbonising temperature employed. These figures will, no doubt, be found useful for the purpose of comparison, and they are reproduced in Table 46. The figures are reckoned on the dry basis.

Table 47 gives the distillation tests of several types of tar, and it will, no doubt, be found useful for making comparisons.

Table 48[2] is interesting in that it enables a comparison to be made between high and low heat horizontal tar, Dessau vertical retort tar, and coke oven tar.

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[1] "Tar and Liquor." See *Gas World*, April 18th, 1914, pp. 523-527.

[2] "Some features of Carbonisation and By-product Recovery," J. Thorp. See *Gas World*, May 3rd, 1919, Coking Section, p. 12.

It is the opinion of many that paraffinoid tars "crack" more readily than benzenoid tars while undergoing the process of destructive distillation, and with this opinion the author agrees. Reginald Cross[1] carried out some experiments with the object of proving this contention, and in Table 49 are given some figures obtained by this worker.

TABLE 46

WORKS SAMPLES FROM SALES TANKS

Conditions.	Specific Gravity.	Free Carbon. Per cent. by weight.	Percentage by volume.						
			Up to 100° C.	100° to 130° C.	130° to 170° C.	170° to 230° C.	230° to 270° C.	270° to 330° C.	Above 330° C. (Pitch)
Horizontal retorts.									
Two ascension pipes, charges $5\frac{3}{4}$ cwts. in 6 hours, 1800° F.	1·182	16·4	1·4	1·9	0·3	14·7	9·5	11·3	60·9
Two ascension pipes, charges $6\frac{1}{2}$ cwts. in 6 hours, 1950° F.	1·191	20·3	2·1	1·3	0·1	12·5	10·8	8·1	65·1
Two ascension pipes, charges mostly 12 cwts. in 12 hours, 1900° F.	1·129	13·9	2·0	0·6	0·4	18·9	12·8	13·6	51·7
One ascension pipe, charges $9\frac{1}{2}$ cwts. in 8 hours, 1950° F.	1·200	20·2	1·5	0·7	0·8	12·7	11·1	8·5	64·7
Inclined retorts.									
One ascension pipe, charges mostly 6 cwts. in 6 hours, 1900° F.	1·176	19·4	2·0	0·7	0·4	15·1	11·2	11·4	59·2

During the period of the Great War (1914–1918) the subject of increasing the yield of toluene from tar received a great deal of attention on account of the importance of this material in the manufacture of munitions of war. One of the most interesting investigations in this connection is that of G. Stevenson,[2] who finds that the mixing of limestone with coal prior to charging into the retorts increases the yield of toluene from the tar obtained. Some of the results he secured are set out in Table 50.

From time to time "free carbon" has been a subject of interest and speculation as to its composition. The result of many qualitative experiments has caused the author to come to the conclusion that this material is not pure or elemental carbon, but a mixture of this material with other bodies of a high carbon content. This conclusion is supported by the work of Hubbard and Reeve,[3] who have made several ultimate analyses of "free carbon" with the results shown in Table 51, and also by the work of J. M. Weiss.[4] The result of an analysis of average "free carbon" from coal tars made by this worker is given in Table 52.

[1] *Gas World*, February 24th, 1917, p. 159.

[2] *Gas World*, January 29th, 1916.

[3] *Proc. Amer. Soc. Testing Materials*, 2 (1911), 665.

[4] *Jour. Indust. and Eng. Chem.*, Vol. 6, No. 4, p. 279. April, 1914.

TABLE 46 (*continued*)

COAL TEST PLANT EXPERIMENTS

Conditions.	Specific Gravity.	Free Carbon. Per cent. by weight.	Percentage by volume.						
			Up to 100° C.	100° to 130° C.	130° to 170° C.	170° to 230° C.	230° to 270° C.	270° to 330° C.	Above 330° C. (Pitch).
Horizontal retorts.									
Coal " A " (Derbyshire)—									
(1) Coalite conditions	1·120	7·6	3·7	3·2	0·1	18·4	10·9	13·2	50·5
(2) Ordinary conditions, 6·4 cwts. in 6 hours, 1980° F.	1·190	19·1	1·5	1·5	0·4	10·9	10·7	10·3	64·7
Coal " B " (Yorkshire)—									
(1) 4·54 cwts. in 6 hours, 1640° F.	1·160	—	12·7	2·1	1·6	4·8	16·1	12·5	50·2
(2) 4·87 cwts. in 6 hours, 1975° F.	1·234	27·5	3·5	1·1	0·8	7·9	7·3	7·6	71·8
Light and heavy charges.									
Coal " C " (Derbyshire)—									
(1) 6·41 cwts. in 6 hours, 1980° F.	1·190	19·1	1·5	1·5	0·4	10·9	10·7	10·3	64·7
(2) 12·21 cwts. in 12 hours, 2065° F.	1·150	15·9	1·9	1·6	0·4	17·1	11·4	15·5	52·1
Coal " D " (Derbyshire)—									
(1) 6·52 cwts. in 6 hours, 2020° F.	1·211	23·8	1·7	2·7	0·0	8·9	10·0	7·7	69·0
(2) 9·59 cwts. in 9 hours, 1980° F.	1·151	15·5	3·9	3·2	1·4	14·1	10·2	11·5	55·7
Coal " E " (Derbyshire)—									
(1) 6·49 cwts. in 6 hours, 1990° F.	1·177	20·5	2·4	5·1	0·3	13·2	12·0	7·8	59·2
(2) 13·41 cwts. in 12 hours, 1990° F.	1·107	—	1·6	0·8	0·1	21·7	11·0	14·2	50·6
Wet and dry mains.									
Coal " F "—									
(1) Wet main, 6·41 cwts. in 6 hours, 1980° F.	1·190	19·1	1·5	1·5	0·4	10·9	10·7	10·3	64·7
(2) Dry main, 6·51 cwts. in 6 hours, 1980° F.	1·210	27·7	0·7	0·6	0·5	8·0	9·1	5·2	75·9
Coal " G "—									
(1) Wet main, 6·41 cwts. in 6 hours, 1920° F.	1·158	18·9	2·9	0·7	1·2	14·5	9·8	11·8	59·1
(2) Dry main, 6·35 cwts. in 6 hours, 1965° F.	1·215	26·8	1·0	0·9	0·4	8·6	8·7	10·2	70·2
Poor and rich coals.									
(1) Derbyshire, 6·23 cwts. in 6 hours, 1990° F.	1·190	24·6	1·4	0·9	0·2	12·2	10·3	10·9	64·1
(2) Yorkshire, 6·49 cwts. in 6 hours, 2025° F.	1·229	28·4	1·6	1·0	0·3	10·2	9·1	7·9	69·9
(3) Wigan cannel, 5·74 cwts. in 6 hours, 2040° F.	—	11·4	4·6	3·9	1·4	5·2	8·9	4·6	71·4
Dessau vertical retorts.									
(1) Coal " H " (Yorkshire)	1·14	4·47	0·6	0·4	0·4	12·0	10·7	13·1	62·8
(2) Horizontals for comparison, 6·44 cwts. in 6 hours, 2070° F.	1·216	25·8	1·7	1·4	0·1	10·0	9·2	7·9	69·7
Woodall-Duckham vertical retorts.									
(1) Coal " I " (Derbyshire)	1·110	3·8	1·7	2·9	0·5	12·2	11·8	8·6	62·3
(2) Horizontals for comparison, 6·41 cwts. in 6 hours, 1910° F.	1·190	19·1	1·5	1·5	0·4	10·9	10·7	10·3	64·7

TABLE 47[1]

	High Temperature Tar (Horizontal).		Lower Temperature Tar (Horizontal—Country).		Vertical Tar.		Producer Tar.		Suction Gas Tar.	
		S.G.		S.G.		S.G.		S.G.		S.G.
S.G. . . .	1·190	—	1·130	—	1·065	—	1·110	—	1·058 (approx.)	—
Water . . .	2·5% wt.	—	2·5% wt.	—	4% wt.	—	6·5% wt.	—	19·7% wt.	—
170° C. . . .	1·25% wt.	·912	3·1% wt.	·891	2·7% wt.	·858	·8% wt.	?	1·3% wt.	?
230° C. . . .	8·5% wt.	1·000	14·3% wt.	·969	20·9% wt.	·945	·6% wt.	?	3·0% wt.	·899
270° C. . . .	10·93% wt.	1·025	12·3% wt.	1·012	12·6% wt.	·989	6·7% wt.	·955	11·0% wt.	·959
350° C. . . .	6·05% wt.	1·055	5·4% wt.	1·046	19·3% wt.	1·025	16·8% wt.	1·007	19·3% wt.	1·008
Pitch . . .	69·22% wt.	1·28	61·4% wt.	1·24	40% wt.	1·20	67·0% wt.	1·21	43·5% wt.	1·17
Soda extract (total distillates) . .	12%	—	17%	—	22%	—	18%	—	19%	—
Acid extract (total distillates) . .	3·5%	—	7%	—	5%	—	1%	—	12%	—
Free carbon in tar .	16·35%	—	8·3%	—	1·11%	—	—	—	—	—
Free carbon in pitch .	29·45%	—	16·4%	—	10%	—	—	—	—	—
Vol. matter in pitch .	61·9%	—	61·5%	—	78·8%	—	75%	—	84·8%	—
Melting point of pitch	164° F.	—	138° F.	—	166° F.	—	175° F.	—	128° F.	—
Twisting point of pitch	135° F.	—	110° F.	—	134° F.	—	Above 140°F.	—	105° F.	—

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[1] Reginald Cross, *Gas World*, February 24th, 1917, p. 159.

TABLE 48

	Low Heat (Horizontal Tar).		High Heat (Horizontal Tar).		Coke Oven Tar.		Dessau Vertical Retort Tar.	
Ammonia water, gallons per ton of coal	4·94	% NH_3 ·55	10·53	% NH_3 ·35	6·59	% NH_3 1·58	3·25	% NH_3 ·38
		sp. gr.		sp. gr.		sp. gr.		sp. gr.
Crude naphtha ,, ,, ,,	10·56	·896	6·60	·933	3·40	·980	4·26	·886
Carbolic oil ,, ,, ,,	22·92	1·005	4·03	1·005	11·10	1·005	62·26	·993
Creosote oil ,, ,, ,,	38·36	1·04	33·03	1·040	49·44	1·04	8·95	1·040
Blue oil ,, ,, ,,	39·37	1·080	17·02	1·084	18·20	1·080	16·91	1·072
Pitch in lb. ,, ,,	1,032·00	—	1,495·20	—	1,308·00	—	1,260·00	—
Lost in distillation ,, ,, ,,	8·20	—	9·43	—	10·10	—	17·23	—
	1 ton		1 ton		1 ton		1 ton	
The above yielding :—								
Tar acids, gallons per ton of tar	10·20		3·23		7·44		14·00	
Crude pyridene ,, ,,	·84		·25		·35		1·96	
Benzole ,, ,,	1·90		1·45		·20		1·06	
Toluole ,, ,,	1·24		·61		·10		1·17	
Solvent naphtha ,, ,,	1·82		·89		·72		2·46	
Per cent. "free carbon" ,, ,,	8·60		17·50		7·20		2·18	

TABLE 49

Tar tested.	High temperature tar (horizontal).	Low temperature tar (horizontal).	Vertical retort tar.
" Free carbon " in tar	16·35%	8·3%	1·11%
" Free carbon " in pitch	29·45%	16·4%	10·00%
If no increase in " free carbon," due to "cracking," the amount in the pitch should be .	24·70%	13·5%	2·80%

TABLE 50

Quantity of Tar taken, 9000 c.c.

	Normal carbonisation with " C " washing.	Limestone used. No "C" washing.	Limestone used and also " C " washing.
Crude naphtha .	176 c.c.	320 c.c.	508 c.c.
Middle oils . .	720 c.c.	850 c.c.	800 c.c.
Toluene in tar, lbs. per ton of coal	0·27	0·41	1·01

TABLE 51

	From	To
Carbon	90·17	94·26
Hydrogen	2·59	3·31
Oxygen	1·81	5·91
Sulphur	0·50	1·78

Nitrogen—no trace upon a qualitative test.

TABLE 52

Carbon	89·85
Hydrogen	3·30
Nitrogen	1·10
Oxygen	3·13 (by difference)
Sulphur	1·28
Mineral ash	1·34

The inference drawn by Weiss from many of his experiments is that the solvents used actually enter into combination with some of the constituents of the tar, and that the longer the time allowed for the solvents to act the larger the amount of compound formed and the greater the amount of insoluble residue (" free carbon ") obtained.

It is highly probable that " free carbon " plays some part in the water-carrying property of tar, and this may be due to the emulsifying power which carbon possesses. For particulars of the action of carbon black as an emulsifying agent the original work of Schlæpfer[1] and also of Moore[2] should be consulted. W. W. Odell[3] considers that " free carbon " is the emulsifying agent in the case of water-gas tar emulsions, and that these emulsions are of the type in which water is the inner phase.

According to Reginald Cross[4] the effect of adding " free carbon " to a tar which is low in that substance is to increase the distillates up to 230° C.; but almost exactly at the expense of those following, the percentage yield of total oil obtained from the tar employed being the same in each case. This worker added to a vertical retort tar which contained only 1·11 per cent. of " free carbon " a further 10 per cent. of lamp black. This was added in small quantities, and well shaken up after each addition. Table 53 gives the results of the distillation, the last column being added by the writer.

TABLE 53

	90 per cent. tar and 10 per cent. carbon.			Same tar distilled alone.			Results shown in Col. 1 calculated to original tar.		
	Per cent. by weight.			Per cent. by weight.			Per cent. by weight.		
H_2O	4			4					
170° C.	4·6	23·7	50	2·7	23·6	55·5	5·11	26·33	55·5
230° C.	19·1			20 90			21·22		
270° C.	10·1	26·3		12·6	31·9		11·22	29·22	
350° C.	16·2			19·3			18·00		
Pitch	45·1			40					

Table 54, due to J. Morris Weiss, gives the percentage of " free carbon," specific gravity, and the coefficient of expansion of a number of tars. The figures were determined on dry tars.

TABLE 54

Kind of Tar.	" Free Carbon " per cent.	Specific Gravity at 60° F.	Coefficient of Expansion for ° F.
Water gas . .	1·04	1·073	·0003750
,, . .	1·08	1·090	·0003550
Gasworks coal .	16·67	1·203	·0003125
,, ,, .	18·53	1·205	·0003125
,, ,, .	27·50	1·249	·0003100
,, ,, .	33·17	1·296	·0002700
Coke-oven coal .	8·97	1·185	·0003375
,, ,, .	5·27	1·193	·0003350
,, ,, .	4·04	1·178	·0003300
,, ,, .	6·72	1·195	·0003250
,, ,, .	6·65	1·197	·0003125
,, ,, .	9·10	1·203	·0003125
,, ,, .	19·06	1·258	·0003075
,, ,, .	15·02	1·231	·0003050

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[1] *Jour. Chem. Soc.*, 113, 522. 1918.

[2] *Jour. Amer. Chem. Soc.*, 41, 940. 1919.

[3] *Gas Jour.*, 1922, 158, 152–153.

[4] *Gas World*, February 24th, 1917, p. 159.

Table 55 will, no doubt, be found useful for calculation purposes.

TABLE 55

°Tw.	Sp. Gr.	Gallons per ton.
14	1·070	209·34
15	1·075	208·37
16	1·080	207·40
17	1·085	206·45
18	1·090	205·50
19	1·095	204·56
20	1·100	203·63
21	1·105	202·71
22	1·110	201·80
23	1·115	200·89
24	1·120	200·00
25	1·125	199·11
26	1·130	198·23
27	1·135	197·35
28	1·140	196·49
29	1·145	195·63
30	1·150	194·78
31	1·155	193·93
32	1·160	193·10
33	1·165	192·27
34	1·170	191·45
35	1·175	190·64
36	1·180	189·83
37	1·185	189·03
38	1·190	188·23
39	1·195	187·44
40	1·200	186·66
41	1·205	185·89
42	1·210	185·12
43	1·215	184·36
44	1·220	183·60
45	1·225	182·85

According to the Annual Reports of the Chief Inspectors of Alkali Works, the amount of tar distilled in the United Kingdom during the year 1920 is as follows :—

United Kingdom (not including Scotland).

	Tons.
Distilled in gas and coke oven works .	1,450,535
,, ,, other works . . .	117,788

Scotland.

Distilled in gas and coke oven works .	141,546
,, ,, other works . . .	103,551
	1,813,420

Allowing that one ton of tar contains 190 gallons, then this amount is equivalent to 344,549,800 gallons.

From the reports on the year 1921 it appears that less tar was distilled in the United Kingdom during that year than on the previous year. The figures are given below :—

	Tons.
Tar distilled in gasworks and coke oven works	1,013,245
,, ,, other works	40,008
	1,053,253

Taking 190 gallons per ton of tar then this figure represents 200,118,070 gallons.

CHAPTER IV

LAY-OUT OF TAR WORKS

Although at the present day there is a tendency to decentralise the process of tar distillation, the producer working up his own tar, and with this tendency the probability of erecting further large centralised tar distilleries is reduced, the author thinks it is very important that the student or work's chemist who wishes eventually to fill a position as chemical engineer or works manager, should possess some knowledge of the lay-out of such a works ; hence this chapter.

The choosing of a site upon which to erect a tar distillery, or as a matter of fact any kind of chemical works, is a very important procedure and one to which very careful consideration should be given. Transport facilities (inward and outward), proximity to source of supply of raw material, local geology, and physical geography are items of great importance in this connection, and if not dealt with properly will stand in the way of efficient and economical working.

It is not always possible to find a site which offers rail, canal or river, and main road transport facilities, but this ideal combination should be kept in mind. The frontispiece and Figs. 11, 12, 13 illustrate ideal sites. Instances may occur in which the matter of carriage on raw material make it necessary to forgo one or other of the transport facilities just mentioned ; for instance, a works collecting tar from a number of inland towns in close proximity may have to do without canal or river transport.

In regard to local geology the author's experience leads him to think that this is a matter which is neglected more often than not, and when it is the result is more or less costly repairs or structural alterations. There are positions which possess all that is required in regard to favourable transport facilities to and from the works, upon which it would be very unwise to build ; for instance, if at a moderate depth only there exists a thick strata of peat, soft shaly or slippery clay, or shifting gravel, especially when one or more of these occur on the side of an old valley ; or if the underlying strata is cavernous. In the majority of cases, however, a more or less faulty condition of the underlying strata can be dealt with satisfactorily, provided the trouble is taken to learn all that is necessary of the surface geology before commencing to put up a building or to erect a unit of plant.

A number of years ago a case came before the author in which some large stills were standing idle owing to the underlying strata shifting on account of the superimposed weight. This movement had caused the stills to lean some 12 inches out of plumb, making connections with the existing condenser worms practically impossible, cracking the flues, destroying the producer gas inlets, and rendering connections with the pitch coolers a difficult matter. On making an investigation it was discovered that the underlying strata consisted of spongy clay with gravel, to a depth of nearly 20 feet; the stills were, in fact, erected over a portion of an old river bed. Only ordinary brickwork foundations with footsteps had been put in. Later some new plant was erected upon this site, and the difficulty was overcome by the use of a concrete raft or grillage upon which the whole lot was floated.

If large storage tanks, chimney stacks, reaction towers, steam boilers, etc., are erected upon unsuitable land, subsidence will take place at some time or other, bringing in its train trouble due to cracks, strained joints or seams, etc., and necessitating costly repairs and often serious delays.

The settling of a building, especially if unequal, will not only cause serious cracks in the walls, floor, and roof, but bring about a considerable amount of trouble in connection with stationary and moving plant. For instance, stills will be thrown out of plumb and difficulties will arise in regard to making tight steam, oil, and vapour pipe connections, and especially will this be the case with those stills fitted with fractionating columns; pipe lines will be strained and leaky joints will result; lines of shafting will be subjected to strain, and not only will the joints suffer, but the effect may be felt in the bushes of hangers and wall brackets. Belt drives will be thrown out of alignment, and wear and tear on the belts increased; and in all these cases, and in others not mentioned, there will be a loss in efficiency.

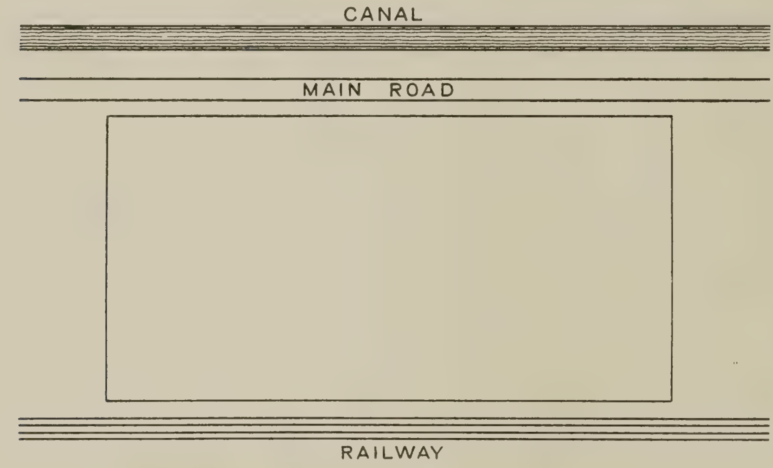

Fig. 11.—An Ideal Site.

Neglect of the physico-geographical conditions also leads to trouble in some instances; for example, when the land is situated on the banks of a tidal river and lies at a level below that of unusually high spring tides. The author knows of cases in which the land covered by works is at a level below that of ordinary high-water mark; the river running between made banks. In the event of an extra high tide produced by wind when the sun and moon are in conjunction, the water overflows the banks and floods these works, often causing damage to machinery and plant, and bringing about a loss of material by floating it away.

The possibility of extending the works should not be lost sight of, and when arranging the various units of plant an allowance of space should be reserved in each case, upon which a new piece of plant can be erected when the necessity arises.

Another very important matter for consideration is that of water supply. A very considerable quantity of water is used in a tar distillery for steam raising, for condensing purposes, and for washing, and water from a river is not always suitable. In practically all industrial centres the water of rivers is far from pure, both from the point of view of contamination by waste effluents and of suspended mud content, and in the case of tidal rivers of sodium chloride.

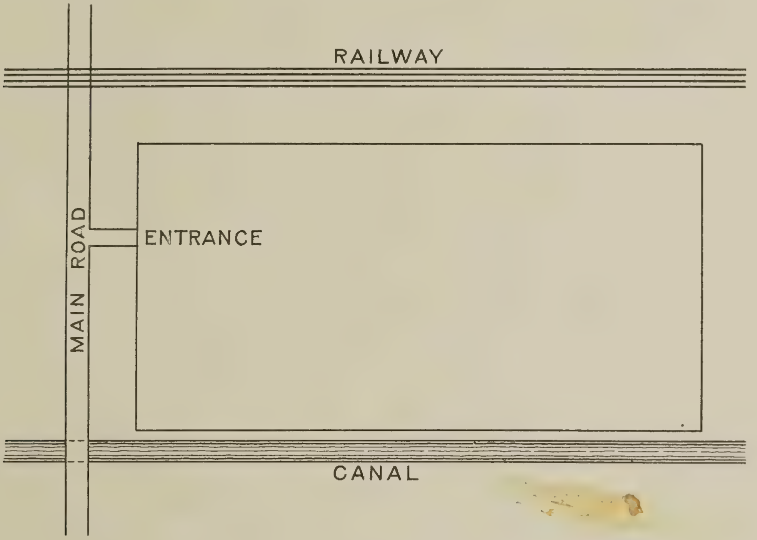

Fig. 12.—An Ideal Site.

The purest water obtainable must be supplied to the steam boilers and used for washing benzoles, etc. In the former case the choice is generally between town water and water from a bore made on the works, and in the majority of instances it is advisable to soften the water prior to use. Water for washing purposes need not be softened, but that from a bore is best to use as it is much colder than town water during the summer time, and this is a matter of importance when washing the lighter coal tar oils; and well water is generally much cheaper. Water from a bore is also best for condenser purposes from a temperature point of view, but river water can be used if it is free from corrosive substances and mud; town water is too expensive. A situation may arise in which it is necessary to reuse the condenser water, and in a case like this a small water cooler and storage tank will be required. Care must be taken that the well above the bore, if one is provided, is properly lined in order to prevent contaminated water from leaking in. The author knows of one instance in which drainage water from an ash heap gained access to a well, and of another in which the well became contaminated owing to creosote leaking in; the soil around having become saturated with creosote due to leaky mains (a common occurrence in some works).

How boiler ashes, slurry and effluents are to be dealt with is another matter of vital importance, and due regard must be given to it, as otherwise serious trouble may ensue shortly after the works has started up. The plan of sending waste solid matter (ashes, "pyridine mud," "lime mud" from causticisers, etc.) to a "tip" may turn out to be a very expensive one, especially if the "tip" is a great distance from the works, or the owner finds that he has the proprietor of the works at his advantage. It may be necessary to provide sufficient land upon which to "shoot" these materials, and if this is the case the area should be large enough to suffice for, say, forty years. The author is acquainted with a works in which they centrifugalise all their slurry to reduce the water content; that from the causticising plant yielding very weak caustic liquor which can be put through the plant and usefully employed. All effluents must be suitably treated before running them into sewers or streams and means must be provided for carrying out this process.

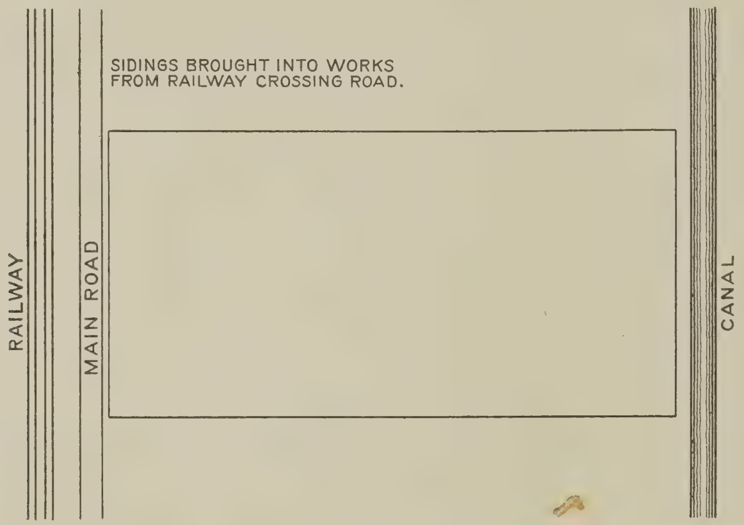

Fig. 13.—An Ideal Site.

In choosing a site the matter of proximity to land under cultivation or the nearness to a residential quarter of a town must receive particular attention, and a clear understanding with the owners of property should be come to before purchasing the site.

All plants which require a steam supply should be placed as near to the steam boilers as possible, and both the boilers and the steam pipes should be covered with an efficient non-conducting material. In the author's opinion compressed magnesia, which is supplied in sections, is the best material to use. It is not wise to employ brickwork or similar impervious coverings for boilers, as the existence of any leakage or dampness beneath them cannot be detected, and serious corrosion may result, owing to the leak not being discovered for some length of time. The boilers should be erected inside a good brick building, well roofed and floored, and not under a corrugated iron shed or in the open.

Sometimes it is necessary to build underground the main flues to the chimney shaft from the steam boilers and tar stills, and in this case care must be taken to do the work properly and to see that the ground is in good condition and not liable to become saturated with water. Water leaking into flues will soon damage the brickwork and may necessitate heavy repairs probably at a very inconvenient moment. Of course, flues are best built above ground, but in many cases this is not possible as they may be in the way. This difficulty can be overcome in most instances by attaching a small chimney to the battery of tar stills and another to the steam boilers.

The disposition of the lines of railway throughout the works must receive careful consideration. One siding should run alongside the boiler house and also the producers if these are to be installed, so that coal can be delivered into the bunkers with facility. Another, consisting of a double line of metals, is required for the pitch bay, and further sidings are necessary for loading and unloading tar oils such as coke oven oils, crude naphtha, crude benzole, benzoles, naphthas, tar acids, creosotes, etc., both in barrels and in bulk, dealing with tar and with chemicals used in the industry, such as sulphuric acid, nitric acid, caustic soda, soda ash, etc.

For the unloading and loading of benzoles and other tar oils in bulk it is an advantage to employ a cylindrical measuring tank, and this applies especially in regard to filling and emptying keels or lighters ; too much reliance should not be placed upon the figures given for the carrying capacity of these vessels.

Pitch is loaded into wagons by means of skeps and a crane, or by a mobile elevator, liquid products loaded or unloaded by a sling and crane or by a mobile barrel elevator if in barrels, or by the use of a stand pipe if filled into tank wagons. The emptying of tank wagons is done by coupling up the cock underneath the wagon to a pipe leading to the suction end of a pump, or if the tank wagons are specially constructed by means of air pressure.

If the works is large enough it is wise to erect a central pumping station, and in any case steam-driven pumps should be employed. There is a danger of fire if motor-driven pumps are used, owing to inflammable vapours coming in contact with the sparks generated between the commutator segments and the brushes of the electric motor.

Flexible pipes of steel, up to 12 inches in diameter, are used for loading and unloading tar and creosote from lighters, but it is best to employ wrought-iron mains for tar acids and the lighter tar oils.

In the case of sulphuric acid it is better to deal with this in bulk rather than in carboys. It is possible for the makers to send it to the works in 10-ton steel railway tank wagons and then it can be run by gravitation direct from the wagon into a wooden tank lined with 8 lb. lead. From this tank it can be elevated to the plant supply tanks by means of an acid elevator made of " Narki " or other suitable metal, or by a centrifugal pump made of the same metal (" Narki "). If desired the storage tank can be elevated and used for the plant supply tank and the acid pumped direct from the wagon into it. Lead or " Narki " metal pipe lines must be employed.

At times it is necessary to put in a temporary pipe line, and often hurriedly. In cases of this nature, and, it might be added, when putting in permanent mains, the writer can strongly recommend the use of the Victualic Joint. By employing this joint instead of flanges or screwed socked joints, a very considerable saving in time is secured and there is no risk of leaking. Also on account of the flexibility of this joint a pipe line can be laid on a ground surface of any contour without risk of straining and its accompanying evil, leaking, taking place. There is no need to fit expansion joints to long lengths of steam main or to pipe lines which are to carry hot fluids, the construction of the joint provides for expansion and contraction.

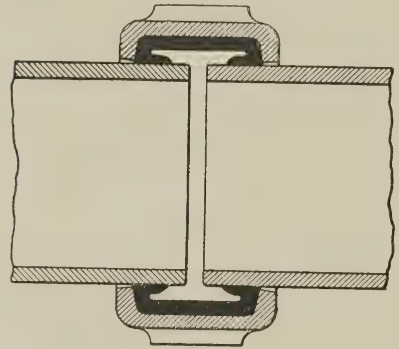

FIG. 14.—"A" TYPE VICTUALIC JOINT.

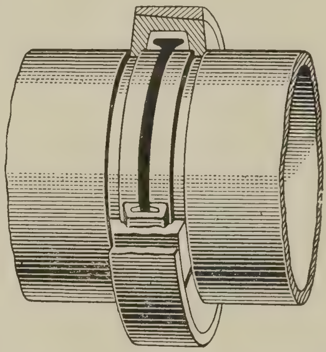

FIG. 15.—" B " TYPE VICTUALIC JOINT.

Of the several types of Victualic Joint offered by the manufacturers, the " B " type (located) is the best to use for permanent mains, whilst the " A " type (floating) will be found suitable, in many cases, for those of a temporary nature. If the latter kind of joint is used it is necessary to anchor the pipe line in places, say, at the bends, elbows, etc. Sectional diagrams of the " A " and " B " types are shown in Figures 14 and 15. It is sound practice to paint pipe lines which carry steam and various liquids in different and distinctive colours, and in cases in which a risk of a mistake occurring exists valves should be labelled.

The matter of shunting must not be overlooked as it is one of considerable importance, and if not properly considered at the outset will soon lead to non-economical working of the factory. Motive power can be supplied by (a) horses, (b) small locomotives, and (c) locomotive cranes. Shunting by means of horses should be avoided if possible ; it is slow, uncertain, and expensive. The employment of locomotives is to be recommended if the size of the works allows of it, and at least two should be put into commission ; if one only be installed an awkward situation will arise when it needs overhauling or repairing. It is not the best plan to use locomotive cranes for the entire shunting, but for moving trucks in the proximity of the pitch bay they come in useful, serving the dual purpose of loading the trucks and removing them; and the crane can be shifted from point to point alongside the bay, thus minimising the distance the skeps have to be trollied to bring them underneath the wire rope of the crane.

Weighbridges must be erected on the sidings to deal with inward and outward goods, and it is important that one of these machines, large enough to deal with a 3-ton motor lorry, is erected at the main-road entrance to the works, at which, also, there should be a small weigh office.

Runways carrying chain-blocks and also small transport cars can be erected with advantage in various parts of the works. These pieces of apparatus will be found useful in lifting and carrying drums of caustic soda, sacks of soda ash, etc., and, in manipulating portions of plant undergoing repairs the time and expense of erecting a scaffold will often be saved.

Sufficient space must be reserved for storage tanks for raw materials, for virgin products and also for finished materials. The positions of these tanks should be as far away as possible from the steam boilers and fire-heated stills, and in the author's opinion are best erected above ground and not below as suggested by some. If erected in a vertical position much economy of space is secured, and as most tar oils when fresh from the stills, and often when received from outside sources, contain water in suspension, tanks in this position will allow the water to be separated more easily, especially if the bottom of the tank is slightly dished and a drain cock placed in the middle. In any case a draw-off pipe is fitted to the side of the tank and its centre is arranged 6 inches above the bottom line of rivets. Tanks which are to be used for the storage of salty creosote, and heavy oils liable to hold water in the emulsified state, are best provided with a closed steam coil and covered with lagging on the outside. The subject of large storage tanks for tar will be dealt with in Chapter V.

It is necessary to light the works adequately, and due regard must be paid to fire risks in this connection. Electric light is the most suitable, and filament lamps should be used, each globe being enclosed in an outer glass cover as an extra precaution. The leads must be well insulated and carried in a first-class quality of metallic conduit, and the switches placed in positions away from inflammable vapours; when thrown in and out of clutch switches are liable to spark. The main switch board and fuse boxes are best situated in the office building. Especial care must be taken over the lighting of the benzole and naphtha house; the safest place for the lamps is outside the building in front of windows with good reflectors at their backs, and the switches are fitted outside the building also. For the temporary lighting of dark corners, etc., and to enable the workmen to more easily read hydrometers, etc., during the night shifts and on dark winter days Davy safety lamps must be provided, and these lamps find a use on all occasions for illuminating the inside of tanks, stills, etc., undergoing inspection or repairs. It is wise to properly earth the benzole and naphtha stills to avoid risks of fire by static discharges.

Not on any account must the chemical and physical laboratories be overlooked; in fact, these buildings, their equipment and staff should be reckoned among the most important assets of the works. Laboratories for plant control and analytical work and for research work are necessary if the owners of the works wish to carry on along the path of progress. The amount of uninvestigated problems in connection with the plant used in the distillation of tar and tar products, the tar itself, and the materials obtained from it, is very large, and in the employment of well-trained research chemists, chemical engineers, and physicists by tar works owners money is being well spent. Proof of this contention is found in the fact that some of the large tar works in this country and in the U.S.A. have for some years past had research laboratories and a staff of research workers attached to the establishment. The design and fitting up of the laboratories and purchasing of the equipment ought to be left to the appointed head of the laboratory staff.

The laboratories, a drawing office, and the works and general offices can be conveniently included in one block of buildings, and all the rooms must be well lighted, properly heated, and ventilated. An efficient telephone system ought to be installed connecting up the laboratories, chemical engineer's office, drawing office, engineer's and blacksmith's shops, stores and the various departments of the works with the works manager's office. The instruments of the public telephone service are best enclosed in sound-proof boxes and not fitted in the open office. The duty of installing first-class filing and other labour-saving systems will naturally fall upon the heads of the commercial staff. A cloak room, cycle store, and lavatory accommodation for males and females are other necessities which must not be forgotten, and it will also add to the efficient working of the staff if a room be set apart and properly equipped for the partaking of meals. The need of a works library of books of reference dealing with both scientific and commercial subjects is almost always overlooked, and much needless loss of time and money occurs in most works, many times in a year, owing to the inability of one or other of the staff being able to turn up some important point at a moment's notice in order to settle a dispute, to assist over a difficult problem, or to enable the analytical or research chemist, the chemical engineer, the physicist or the engineer, to make necessary references on the spot instead of waiting until the evening to search in a public library, if there is one near at hand, and if the necessary book is on its shelves.

A drawing office is a very useful adjunct to a tar distillery; in the author's opinion it is a necessity, even if the chemical engineer and the chief engineer, who ought to be qualified men, have to do their own drawing. In a large works this should not be the case, but one or more trained draughtsmen employed. Improvements or repairs to existing plants, the erecting of new plant, laying of mains, etc., should not be carried out without first putting on paper details to scale. It is cheaper to make alterations on the drawing-board than on the plant in the works! The design of new plant to work out new processes or improve old ones will require the services of the draughtsman also.

The need of well-equipped engineer's and blacksmith's shops will be quite evident, and in order to secure efficiency these shops must be staffed with good men.

The engineer should be a thoroughly trained man, and his staff of fitters and blacksmiths and boilersmiths ought to be of the best. Much money can be lost by employing badly trained men. If the works is large enough an assistant-engineer can be with advantage added to the staff. It is absolutely necessary for the well-being of the factory that the chemists and engineers work hand-in-hand.

The equipment of the engineer's shop should not be skimpy, but unnecessary tools must not find a place in it. A hollow spindle centre lathe, a drilling machine, shaping machine, screwing machine, a wet grinder adapted to grinding ordinary tools, and twist drills, taps, and dies, and vices are some of the useful tools required, and with these must be provided all the necessary small tools. This equipment is best arranged by and bought by the engineer, who, if well trained, will exercise forethought and economy when making his purchases.

In the blacksmith's and boilersmith's shop will be required a forge, anvil, and bending machine, also cambering or bending blocks, hammers, chisels, setts, flatters, set hammers, fullers, tongs, caulking tools, rivet sets, punches, drifts, spanners and podgers, centre punches, centering tools, snaps, dollies, clamps, wooden mallets, etc., and one or two electric or pneumatic riveters. Plates can be purchased cut to various sizes, but if the size of the works warrants it a shearing machine will be found a useful addition.

A carpenter and a small carpenter's shop is a very useful addition to a works of large size, but in the average-sized works this is hardly necessary, as wooden structures should be avoided as far as possible in a tar distillery.

Power must be furnished to the workshops, and if possible this is best taken from an electricity service.

Be the works small or large a stores department is required controlled by a reliable storekeeper. In the stores are kept all the engineer's, blacksmith's, and boilersmith's tools which are not in use; labourer's tools, such as ropes, blocks, shovels, picks, wedges, buckets, barrows, brushes, etc.; materials used for repairs and renewals, and so on. An efficient system of dispensing and receiving any of these articles is absolutely necessary. A system which occupies an unnecessary amount of the workman's time in getting out of the stores a required tool, or other article, is as uneconomical as no system at all, and may in the end be found as expensive, or nearly so, as having no stores department.

An exceedingly necessary adjunct to the works is a time-keeper's office, and an efficient system of time-keeping. The office should be in such a position that every workman has to pass it upon entering or leaving the works, and the system of supervision so arranged that a workman cannot record his time and that of several of his mates. There are several good systems of time recording, among them being the Bunday, the Gledhill-Brook, and the International.

A mess-room properly lighted, warmed, and ventilated, with means for cooking and washing-up; good lavatory accommodation with hot and cold water supply; and a cloak-room and cycle shed, ought to be provided for the workmen. These buildings are best situated near the time-keeper's office, but inside the works.

Tar distilleries are very liable to outbreaks of fire, and for this reason an efficient system of fire-fighting must be installed. A certain number of the works and office staff should be trained in the methods of fire extinguishing and how to use the apparatus required for this purpose. Periodic drills and surprise tests are necessary to keep the workers efficient. A good and certain water supply must be provided, and with this end in view an elevated tank of suitable size placed in a position unassailable by fire, and fed by a pump in a similar position, should be erected. This tank can be used for supplying water to the condensers, but it must be always kept full. The position of the hydrants calls for careful consideration, and if this is not given, in a time of necessity it may be found impossible to put one or more into use. Many small fires can be best put out with sand, and it is wise to keep a few buckets of this material in various convenient positions. Patent extinguishers are also very useful in dealing with small fires, and among these the author has used with success apparatus supplied by the Pyrene and the Minimax Companies. In well-constructed works the benzole and naphtha plants are erected in substantial brick buildings, and in order to cope with a fire which has got out of hand, inasmuch as sand or a patent fire extinguisher will not quench it, steam is passed into the closed building by means of a number of jets passing through the walls and controlled by valves on the outside. If steam is promptly introduced at a good pressure the fire is generally "smothered." Smoke helmets may be found useful in dealing with bad fires.

Means of rendering first aid to the injured and of rescuing workmen in danger must be provided. For first aid purposes it is best to set apart a small room in the office or laboratory building. This room should be well lighted and ventilated and in the winter months kept warm. In addition to a very complete first aid equipment, the room must be fitted with hot and cold water supply, sink, and wash-hand basin, and furnished with bowls, towels, nail brushes, stretcher, oxygen bottle and fittings, couch, chairs, and a small table. If the works is large enough a trained nurse is best placed in charge of the room, otherwise it should be required of, say, the chief chemist to take up the duty of first-aider when required. He must, of course, have passed an examination in advanced first aid before taking up the work. It is a wise plan to encourage the members of the office and works staff, and also the workmen, to take up the study of first aid under the auspices of the St. John Ambulance Association.

In regard to rescue work all the workmen on the permanent staff should receive a course of training in this important subject, with frequent revisions, in order to keep the methods of rescue, etc., fresh in their minds. The rescue apparatus must be kept in cupboards near the plant upon which it may have to be used, and all of it must be periodically inspected to make sure that it is in good condition. As a man may be quite insensible when rescued, and as it is necessary to remove him to the ambulance department with the utmost speed, a stretcher is an essential item of the equipment. The kinds of apparatus required and the methods recommended for rescue are dealt with in the appendix.

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CHAPTER V

HOW TAR IS RECEIVED FROM GAS WORKS, ETC.

Tar is delivered to the distillers from the gasworks in railway tank wagons, lighters or keels, tar carts, and, less frequently, the distillery is connected direct to the source of supply by a pipe-line. Examples of the last named are to be found in London, Birmingham, and some other towns. Consideration will not be given here to the construction of the tank wagons and the other vehicles of transport, beyond stating that cylindrical tank wagons are the best to use for tar carriage. A few words, however, on the plant and methods employed for emptying them on their arrival at the distillery is necessary.

It is usual to provide a tar-tip into which these vehicles can be emptied prior to running or pumping the tar to storage tanks, but it should be mentioned that in some cases the tar is run direct into an underground tar storage tank or tar well. The tar-tip for railway tank wagons may be constructed between the railway metals or on the side of the permanent way, but the latter position is perhaps the better, both from the point of view of safety and convenience. A spot should be chosen at a suitable part of the works siding, and, of course, the position should be one which will allow the wagon to pass over a weighbridge first. A hole of sufficient size should be dug between the metals and the bottom well puddled with clay. A covered wrought-iron tank, well coated with a bituminous iron protective solution on the outside and provided with a 14-inch diameter hole and cover, is lowered into the excavation, the sides and top well puddled, and the earth filled in on the top to the sleeper level. The tank may be built of brindled or Staffordshire blue bricks set in cement mortar, or of reinforced concrete, and in both cases the excavation should be well puddled first.

In the author's opinion a wrought-iron tank is the easier to put in and the more suitable for this particular work. The tank capacity should be at least that of a large railway tank wagon ; and the author would add in this connection that he has used with economy, and to great advantage, the tank portions of old railway tank wagons after they have been overhauled. It is, of course, necessary to provide an outlet for the tar and to connect this outlet to a pump. In the case of old railway tank wagons the discharge outlet can be conveniently used, or, if desired, this can be closed, and an outlet cut in one of the sides of the tank near the bottom. As the tar gets very thick in cold weather it is an advantage to use tank wagons provided with a steam coil and to see that a steam main and suitable connections are erected near the tip. Warming the tar will expedite the process of emptying considerably.

As many tank wagons are not fitted with a steam coil, arrangements should be made so that a flexible steam-pipe can be inserted into the tank on its arrival. This is done by connecting to the steam rig a piece of 1-inch or 1¼-inch flexible metallic tubing of sufficient length to allow a foot or two to rest on the bottom of the tank, or else using 1-inch to 1¼-inch steam-pipe, employing the necessary elbows and bends to render the piping flexible and to allow it to adapt itself to the position. Unfortunately, open steam is forced into the tar, and this means that it will become mixed with a certain amount of condensed water. Also there is some risk of noxious vapours escaping from the manhole of the tank ; covering the manhole with sacking will minimise this trouble.

The tip for a tar cart can be constructed in a similar manner to that just described. If it is desired to put in a small tank care should be taken to see that it holds rather more than the volume contained in the cart (approximately 270 gallons), and as to its position, it is advisable to place it as near the emptying pump as possible.

To empty keels and lighters it is necessary to run a pipe line to the canal or river side, and fit suitable flange connections at the end, to which a flexible suction pipe may be attached. The flexible portion may be of wire-bound leather or flexible steel tubing (the latter is the better) ; and the internal diameter of this and the pipe line should be not less than 4 inches—6 inches is preferable.

There are works in existence in which the tar is pumped, as received, direct into the stills, but this is a plan much to be deprecated, and, of course, in large works one which could not be adopted. The chief reasons why tar should be stored are (*a*) to allow much of the entangled liquor (ammoniacal water) to separate, and thus reduce the period and expense of distillation, and (*b*) to keep a sufficient stock in the works to enable it to be run during the "low make" season at the various gasworks from which the supply is drawn. It must be obvious that storage tanks should be of large capacity, and there are tanks now built to hold as much as 1,000,000 gallons. They are constructed above and below ground, and in the latter case are often known as wells.

Storage tanks erected above ground are, if built of wrought iron or mild steel, cylindrical in form, or if constructed of reinforced concrete, cylindrical, cubical, or rectangular solid in shape. Those built below ground are generally constructed of brick or reinforced concrete, and may be cylindrical, rectangular solid, or cubical in shape—the two last-named kinds finding general adoption.

As these tanks are required to hold a very considerable weight of material, often upwards of 3500 tons, it is necessary that a site be chosen where the strata is firm and not likely to subside after a long period of drought, and that a good foundation be put in. If the nature of the strata is not known, it is advisable to make one or two borings at the chosen site. In the case of underground tanks these borings should be carried to a depth greater than that of the depth of the tank and its foundation; for it is quite possible that the ground for some 15 feet or 20 feet below the surface may be quite firm, and then a few feet beyond this running sand or slippery clay may occur. In cases of this nature, if it is not possible to put the storage tank in another position, special precautions must be taken when building the foundation. Should the tank be constructed of brick, concrete, or reinforced concrete, and the foundation built on unsuitable strata, no precaution being taken for this state of affairs, an unequal settling may take place and produce cracking, the results of which would be serious. If the tank is built of iron and subjected to the same unsuitable conditions, the straining produced by unequal settling would bring about leaking at the seams. On firm ground the concrete foundation need not be more than 18 inches thick. In cases where spongy ground has to be built upon, it is advisable to increase the thickness of the concrete and reinforce it with small section angle, tee, or aitch iron, arranged in lattice form. This makes a kind of concrete raft, which will practically do away with all risk of unequal settling.

It is very advisable to build the sides and bottoms of concrete tanks on the reinforced principle. They may be built on the Monier system, in which expanded metal or wire network formed of steel wire is arranged so that the thickest are placed longitudinally and the thinnest transversely, or on the Hennebique system, in which round steel bars are employed; in both cases, of course, the metal-work is surrounded by concrete. The sides of the tank may vary between 8 inches and 12 inches in thickness, according to whether the tank is below or above ground level, or to the size of the tank. One of the best mixings of concrete to use is 4 : 2 : 1 (G. E. Davis recommends 7 : 3 : 1), and it is very necessary that the materials be thoroughly mixed, that an excess or insufficiency of water is avoided, that the water be free from grease or soluble salts such as sodium chloride, sodium sulphate, magnesium chloride, etc., and that the aggregate be non-porous and not contain substances which may exert a chemical action upon steel, and if made up of sand or gravel free from clay or loam. It is unwise to carry out the building of a concrete tank during the winter months when the concrete is liable to become frozen. The wet concrete should be thoroughly punned, best with a pointed rammer, and the centering or casing boards should not be removed until the concrete is thoroughly set. It is absolutely essential that no tar (or creosote) be put into a concrete tank until it is quite set, and a period of several months should be allowed to lapse before putting the tank into use. If a concrete tank is constructed properly it will withstand a liquid pressure of 8½ lbs. per square inch without leaking. The inside of the tank should be rendered with a mixture of 1 of cement and 1 of clean washed sand. It is advisable to puddle round the sides of concrete tanks that are built below ground before filling in the earth. The top of the tank may be constructed of reinforced concrete, wood, or iron plates.

The tar and liquor tanks shown in Figures 16, 17, and 18, have a total capacity of 273,000 gallons, made up of three separate tanks to contain 93,000 gallons of tar, 90,000 gallons of light liquor and 90,000 gallons of heavy liquor, and were built at the new Rome Street Gasworks, Carlisle, to the general designs of Mr. J. E. Blundell, the Gas Engineer and Manager to the Corporation.

The tanks are 63 feet by 63 feet by 12 feet clear depth below roof beams, and are of reinforced concrete throughout, great care being taken to make them absolutely watertight.

This was accomplished by devoting special care to grading, proportioning and placing the concrete, and no special treatment was otherwise necessary.

When the walls were thoroughly dry, as an additional precaution against percolation, the inside walls and bottom were coated with dehydrated tar.

The site upon which the tanks were built was waterlogged from a depth of 4 feet to 5 feet downwards (varying with the seasons) and during construction night and day pumping was necessary, the excavation being kept dry with a No. 6 Pulsometer Pump with one additional pump in reserve in case of breakdown.

One temporary flooding and balancing valve was left in each of the three main compartments, to balance the water pressure in the event of any unforeseen breakdown or stoppage of the pump, as the partly constructed tanks would then have been flooded.

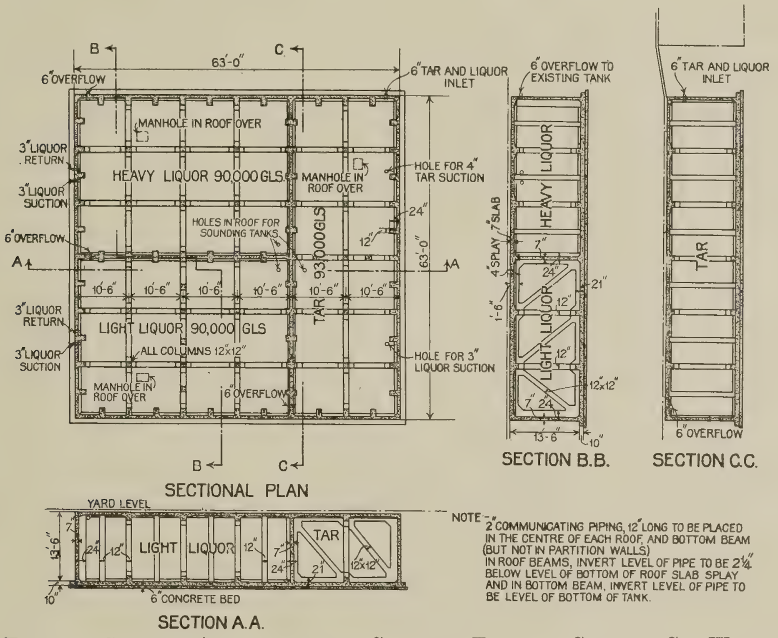

Fig. 16.—General Arrangement of Concrete Tanks at Carlisle Gas Works.

This precaution was justified, as entire cessation of pumping was necessary on one occasion, and the work was flooded without injurious result.

The tanks as a whole are designed as a stiff hollow box to carry water pressure outside with the tanks empty, the whole weight of the finished tanks being arranged to be sufficient to resist flotation.

Figure 16 shows the general arrangement, and Figs. 17 and 18 show the work during construction, with the intermediate and outside walls ready to receive the roof slab.

Each compartment is provided with a manhole in the roof and one hole at the intersection of the internal walls to permit sounding to ascertain the depth of contents at any time.

Holes are left through all roof beams to permit the escape of air, and overflow pipes are provided from the Tar Tank to the Light Liquor Tank, and from the Light Liquor Tank to the Heavy Liquor Tank.

Separate supply and suction pipes are provided to each compartment.

The side walls are 7 inches thick, stiffened by vertical beams spaced 5 feet 3 inches centre to centre and in the bottom and top of the tanks beams running in both directions are spaced at 10 feet 6 inches centres.

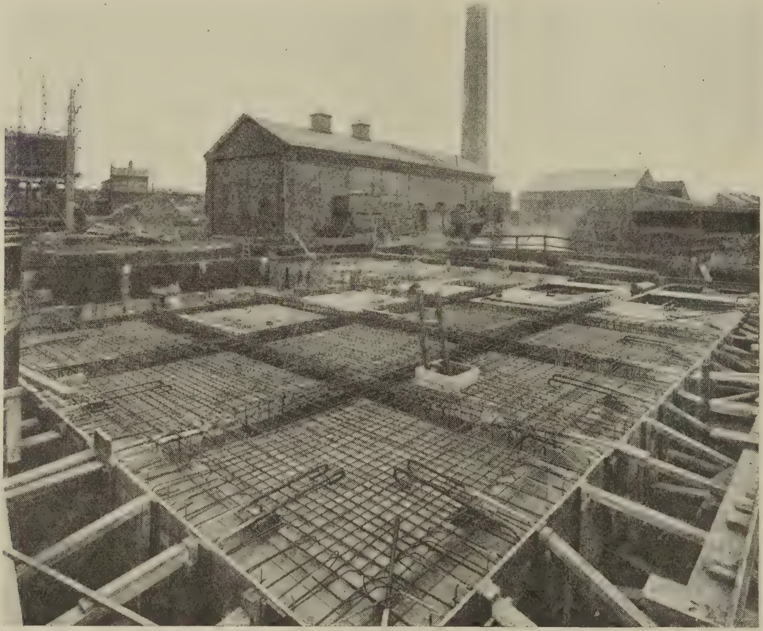

Fig. 17.—Concrete Tanks at Carlisle Gas Works in Construction.

The concrete in the work up to roof level was machine mixed in the proportions of three parts crushed granite ($\frac{3}{4}$ inch down to $\frac{1}{4}$ inch) to $1\frac{1}{2}$ parts of screened and washed sand, to 1 part of "Ferrocrete" Portland cement.

For the remainder of the work where complete watertightness is not so essential, the proportions are changed to 4 of granite, to 2 of sand, to 1 of cement.

The reinforcement throughout consists of round indented steel bars.

The work was executed by Simplex Concrete Piles, Ltd., of 104 Victoria Street, Westminster, to the detail designs and supervision of Burnard Geen, M.Inst.C.E., of 122 Victoria Street, Westminster, the Consulting Engineer to Messrs. West's Gas Improvement Co., Ltd., of Manchester, the Contractors for the new Vertical Retort Installation and sundry other works for the Carlisle Corporation.

Although the author is not aware of any disastrous results accruing through the use of *properly* constructed concrete tanks for the storage of tar or creosote, it is wise to refrain from forming a definite opinion as to their success in this direction until a more lengthy experience of their behaviour is obtained. Internal changes are liable to occur in reinforced concrete, due chiefly to the corrosion of the iron (steel) used for reinforcing, and this may take many years to make itself evident by cracking the structure or otherwise disintegrating it. It should be noted that when iron rusts it increases in bulk ten times, and if rusting occurs in a confined space very considerable pressure results. The corrosion of iron is due to electrolysis, and can be caused (*a*) by substances contained in the concrete, which in the presence of moisture will react upon the steel, or (*b*) by the penetration of aqueous solutions of corrosive salts, such as the chlorides of sodium or magnesium. Cause (*a*) can be eliminated by the careful choice of the aggregate, but the elimination of cause (*b*) is not quite so simple. There are a great number of cases on record of failure of reinforced concrete structures, due to the penetration of aqueous solutions of sodium chloride or of sea water, and in the author's opinion aqueous solutions of ammonium chloride will most likely produce similar results. What

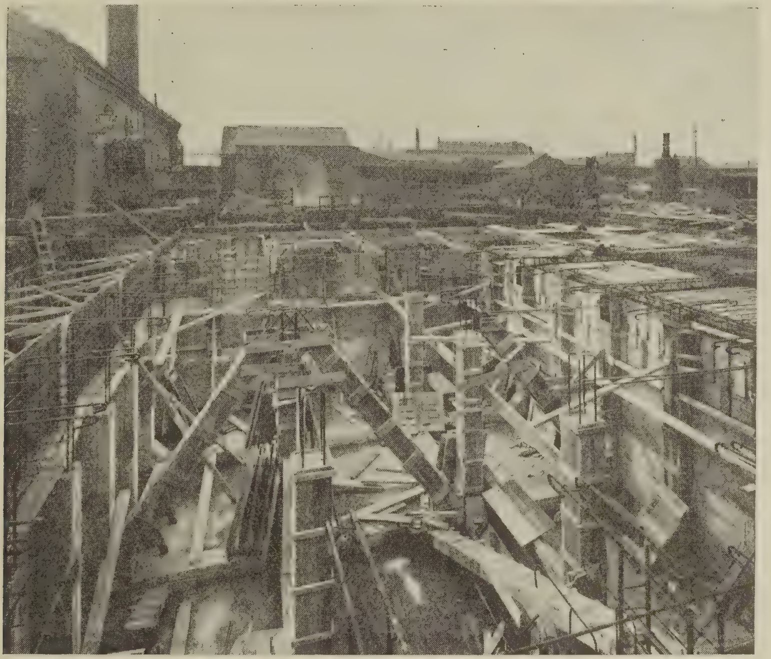

FIG. 18.—CONCRETE TANKS AT CARLISLE GAS WORKS IN CONSTRUCTION.

presumably takes place in the case of sodium chloride is expressed by the following equations :—

(*a*) $NaCl+H_2O \rightleftharpoons NaOH+HCl$.

(Limited hydrolysis of the NaCl.)

(*b*) $\left\{\begin{array}{l} NaOH \rightleftharpoons \overset{+}{Na}+(\overset{-}{OH}). \\ HCl \rightleftharpoons \overset{+}{H}+\overset{-}{Cl}. \end{array}\right.$

(Dissociation of hydrolysis products (*a*) into negative and positive ions.

(*c*) $\overset{++}{Fe}+2(\overset{-}{OH}) \rightleftharpoons Fe(OH)_2$.

(Iron ions which, owing to their electrolytic solution pressure, pass into the water present and combine with the negatively charged hydroxyl ions to form ferrous hydroxide, which is eventually converted into ferric hydroxide by the oxygen dissolved in the solution.)

Experience of the corrosive nature of aqueous solutions of ammonium chloride points to this salt behaving in a similar manner. Now, ammoniacal liquor contains this salt (and other ammonium salts which can exert a corrosive action), and as the material is present in small or fair quantities in tar, and often occurs in creosote, there exists a risk of it penetrating into the concrete in spite of the oily nature of the predominant liquid. Whether this actually takes place can only be proved by experience and careful experiment. In any case it is wise to adopt precautionary measures and render the concrete waterproof. There are several methods of doing this, but in every one care is necessary in its use or else the result will not be successful. Some of these methods are :—

(*a*) Applying three coats of boiling dehydrated tar over the properly set and dry rendering, allowing each coat to soak in thoroughly before applying the next.

(*b*) Painting or spraying over the rendering four coats of an aqueous solution of zinc sulphate ($8\frac{3}{4}$ lbs. to 1 gallon of water). In this case calcium sulphate and zinc hydrate are formed in the pores of the concrete.

(*c*) The use of an aqueous solution of sodium silicate, 2 lbs. to 1 gallon of water, applying four coats and allowing at least six hours between each coat. If this method is employed calcium silicate is precipitated. The author does not recommend this process.

(*d*) Spraying or brushing the concrete with a solution of a fluosilicate, such as magnesium fluosilicate or the double salt of magnesium and zinc. The strength of the solution applied first should be between 10 and 15 per cent., and that of the second solution between 30 and 35 per cent.

It is an unwise plan to run electric mains in proximity to reinforced concrete tanks.

If it is desired to build the tank of bricks, those of a non-absorbent type, such as brindled or Staffordshire blues, must be employed. The bricks should be set in cement mortar, and the joints should not be too thick, about $\frac{3}{16}$ inch, and the tank must not be put into commission before the cement joints are thoroughly set. As the walls are being built up, good puddle should be well rammed round the outer side to a thickness of at least 12 inches. The thickness of the wall should be between 14 inches and 18 inches, and it is advisable to render the inside of the tank with about $\frac{1}{8}$ inch of the cement-sand mixture mentioned in a preceding paragraph. The top of the tank may be built of similar materials to those used for concrete tanks. Iron tanks are sometimes placed below ground, and if this is done it is essential that every care be taken in the riveting and caulking of the seams. It is wise to apply a good thick coat of pure bitumen paint, free from sedimentary matter, to the underside of the bottom and to the outsides of the tank. A concrete foundation should be made at the bottom of the excavation, the thickness of which will depend upon the condition of the ground underneath. Properly made clay puddle must be rammed round the sides before filling in the earth, and the tank may be covered in with a wood or iron roof.

Reinforced concrete and iron tanks are the two kinds usually built above ground, and as the method employed in the construction of the former is the same as for those placed below ground, no further description is needed. The fact that they must be stronger must not be lost sight of. It is desirable, however, to consider briefly the construction of iron tanks. These tanks may be built to contain as much as 1,000,000 gallons, but a very usual size is between 250,000 and 400,000 gallons. As these tanks are erected in the open air, and, therefore, exposed to all conditions of weather, corrosion troubles will rapidly set in if they are not properly covered on the outside and underside of the bottoms with a pure bitumen paint free from sediment. The underside of the bottoms should be covered during erection, and the outsides after completion. It is absolutely essential that good sound work be put into the tanks during their erection, as from the time of completion they are generally full, or partly full, of tar, and this condition will make it exceedingly difficult, if not impossible in many cases, to carry out repairs without first emptying—a very awkward state of affairs to crop up, say, at a busy time.

In all cases the vertical seams must be double riveted, and all seams thoroughly caulked. If the riveting is well done caulking in most cases is unnecessary. Care should be taken that the rivets are not too short. They should be of sufficient length to allow the riveter to snap the tail of the rivet properly, and the height of a finished snaphead should be about three-quarters the diameter of the shank. Mild steel rivets of a good quality should be used; poor quality steel rivets are apt to fracture. Rivet holes should be drilled for preference; in punching holes there is a great risk of an unseen fracture occurring between one hole and another, a condition which may lead up to a serious leak when the tank is put into commission. It is also worthy of note that punched rivet holes reduce the strength of the plate by about 9 per cent. and drilled holes about $1\frac{1}{4}$ per cent.

The sheets of mild steel of which storage tanks are built should be, for preference, pressed into shape, and their thickness should vary, being greater for those plates which are to form the bottom ring than for those it is intended to use for the top and intermediate rings. The bottom plates need not be quite so thick as those of the bottom ring. As examples of the thickness of the various plates used in building storage tanks the two following will prove useful :—

1. The tank is required to hold approximately 300,000 gallons of tar, and in this case the diameter may be 55 feet and the depth 20 feet. A tank of this depth would be built up of four rings, each being 5 feet in width. The thickness of the plates composing the bottom ring should be $\frac{5}{16}$ inch, the plates of the next ring $\frac{9}{32}$ inch, the next $\frac{1}{4}$ inch, and the plates of the top ring $\frac{7}{32}$ inch. A thickness of $\frac{1}{4}$ inch is quite sufficient for the bottom plates. The bottom angle ring should be constructed of $2\frac{1}{2}$ inches by $2\frac{1}{2}$ inches by $\frac{3}{8}$ inch section angle steel, and the top angle ring of 2 inches by 2 inches by $\frac{1}{4}$ inch section angle steel. Double riveted joints, with the rivets having a pitch of 2 inches, are used throughout.

2. In this example a storage tank which will hold approximately 906,600 gallons is chosen. The diameter of a tank of this capacity will be 86 feet, and the depth 25 feet, the shell being composed of six rings. Each ring is built of plates of different thickness, as set out in the following table :—

Ring No.	Birmingham Gauge (B.G.)	Thickness.	lbs. per super foot.
Bottom Ring 1	1	0·3532 in.	14·128
,, 2	2	0·3147 ,,	12·588
,, 3	3	0·2804 ,,	11·216
,, 4	4	0·2500 ,,	10·000
,, 5	5	0·2225 ,,	8·900
Top Ring 6	6	0·1981 ,,	7·924

The plates used for the bottom will be of the same thickness as those composing the top ring, and the angle steel used for the top angle ring will have a 2 inches by 2 inches by $\frac{1}{4}$ inch section, whilst that of the bottom angle ring will be 3 inches by 3 inches by $\frac{3}{8}$ inch. Care is necessary when making the joints, those in the vertical being double riveted (zigzag method) and those in the horizontal being single riveted. The diameter of rivets, pitch, etc., should vary according to the thickness of the plates, but as in the case under consideration the plates of each ring are of a different thickness the rule cannot be adhered to. Under these circumstances a suitable rivet is one of $\frac{11}{16}$ inch in diameter, and in the single-riveted joints a pitch of $1\frac{11}{16}$ inches, with a distance from the centre of the rivets to the edge of the plate of $1\frac{1}{32}$ inches will meet the case. In regard to the double-riveted joints adopting the zigzag arrangement and using rivets of the same diameter ($\frac{11}{16}$ inch), a pitch of $2\frac{3}{16}$ inches, with a distance of $1\frac{1}{16}$ inches from the centre of the rivets to the edge of the plate and an allowance of $1\frac{1}{4}$ inches between the rows of rivets, will give satisfactory results. If it is desired to cover the tank, then plates of No. 12 B.G. (=0·0991 inch in thickness), weighing 3·964 lbs. per super foot, will be found suitable.

Many tanks are not covered, but if a cover is desired, it can be constructed of mild steel sheets of the thickness mentioned in the preceding paragraph or $\frac{1}{8}$ inch in thickness, with the exception of the crown plate and the outer circle of plates which, if $\frac{1}{8}$-inch plate is used, should be of $\frac{3}{16}$ inch. The cover is generally supported by a middle stanchion, on the top of which are riveted radial arms reaching to the circumference of the tank. Two hatches about 3 feet square, provided with *light* cast-iron covers, should be put in the cover on the outer circle plates, and provision will also have to be made for the entry of the tar inlet pipe, and an outlet for air and foul gas. This outlet pipe should be connected to a small purifier box to retain sulphuretted hydrogen, etc.

If the storage tanks are not covered, it is usual to keep about 18 inches of water on the top of the tar to prevent nuisance. It is necessary, however, to remove the water several times during the year, and as it will contain a certain amount of ammonia it should not be run to the drain, but sold as weak ammonia liquor to an ammonia works, or in the event of the tar works possessing an ammonia plant worked up in this. The tar inlet pipe should be so constructed that it reaches about two-thirds the way down the tank. This will avoid agitation of the top liquor and splashing during pumping, when the tank contains a considerable amount of tar. Of course this precaution need not be taken if the tanks are covered. The inlet pipe should be of wrought iron and of a diameter of either 4 or 6 inches. With regard to the outlet pipe for removing the tar the centre line of this should be about 9 inches from the bottom of the tank. This pipe can be made of cast iron, or better of welded wrought iron, and should be about 6 inches in length and of a diameter of 6 inches. It is carefully riveted to the tank and fixed by means of a flange to a best quality cast-iron plug-cock. If preferred a sluice valve can be used in place of a cast-iron plug-cock, but all the fittings must be of iron.

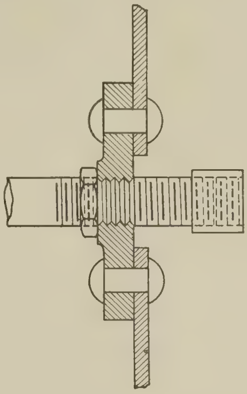

FIG. 19.
A METHOD OF INSERTING STEAM PIPE INTO STORAGE TANKS.

It is a great advantage to provide storage tanks with 2-inch wrought-iron steam coils. They should be put in in the form of a gridiron and supported on rollers. A good method of putting the inlet and exhaust of these coils through the tank side is shown in Fig. 19. The advantage of a steam coil is felt during the winter months, when tar, if it is cold, becomes very difficult to pump, owing to its increased viscosity.

As it is an exceedingly difficult matter to dip a tar tank in order to find accurately the amount of tar and weak ammoniacal liquor it contains, it is advisable, in order to check the dips, to insert a series of $\frac{1}{2}$-inch pet cocks up the side of the tank at a pitch of 3 inches, commencing about 1 foot from the bottom of the tank and finishing about 6 inches from the top.

In choosing tar pumps it is necessary to use care. They must be strong, and all parts which will come in contact with the tar must be of cast iron, in order to minimise corrosion. Pumps for tar of the reciprocating type should be fitted with valves which are mechanically opened and closed, and not with those which are dependent upon the pressure of the liquid or springs for their action. Mechanically operated piston valves, or mitre valves, made of cast malleable iron, are of the correct type. It is important that the valves and the surfaces with which they come in contact (seats, etc.), be made of the same metal, otherwise the risk of corrosion of these parts will exist.

In order to assist in keeping the beat perfect and to prevent the formation of grooves, the ribs of mitre valves should be cast at an incline from the perpendicular so that the liquid on passing through will give the valves a gradual circular motion. It is also necessary to fit tar pumps with cast-iron rams or plungers, or ring-packed buckets ; leather- or canvas-packed buckets are not suitable. In the case of pumps of the rotary type, the same precautions must be taken in regard to the parts which will come in contact with the tar as with reciprocating pumps.

There are several suitable types of pumps on the market, such as the Evans' Cornish, or Reliable, the Worthington and the Tangye of the reciprocating class, and the Douglas Positive Acting Rotary, the Drum Positive Rotary, and the Avamore " Squeegee " pump of the rotary class.

It is a wise plan to employ pipe lines of at least 6 inches in diameter for the conveyance of tar, and they are best constructed of cast iron. The joints must be made with care or else trouble will occur from leaks.

In the author's experience satisfactory results have been obtained from properly made lead wool joints. These joints are approximately twice as strong as run lead joints, and they will withstand considerably more sagging and vibration without leakage. Lead wool joints can be made in any position and under practically all conditions without the anxiety of faulty work and the risk of burning accidents. Another feature in connection with this kind of joint is that of economy ; there is no waste of lead and much less is required, resulting in a saving of approximately 30 per cent.

The Victualic joint is also a very serviceable and economical one to use on tar mains, the leak-proof ring being made of a special composition which will resist the action of tar. A fuller description of this joint is given on page 104.

CHAPTER VI

PLANT USED IN THE DISTILLATION OF TAR

In a tar distillery the pieces of plant subjected to the greatest wear and tear are tar stills, and very careful consideration should be given to the design and construction of them. The portions of a still above the pitch level at the finish of the operation are more or less severely corroded by ammonium chloride and to a lesser extent by ammonium sulphide.[1] The corrosion is much more severe if the still dome, manhole, and charge pipe inlet are wrongly designed, or not properly lagged. The other part of a still which often gives much cause for anxiety is the bottom, which, if not properly built or protected, or if the fireplace is wrongly constructed, may "come down" a few weeks after being put into use.[2]

In the construction of tar stills, wrought iron, mild steel, or sometimes cast iron is used. To employ cast iron is, in the opinion of the author, a great mistake. Although it is now possible to make very large castings in which blowholes are practically absent, freedom from this weakness does not render the metal suitable, as there are other faults. For instance, the thickness of a cast-iron still is much greater than that of one constructed of wrought iron or mild steel, the average of the sides and top being 1½ inches, while the bottom varies between 2 and 2½ inches, the latter thickness occurring at the junction of the run-off pipe (see Fig. 20). This greater thickness of metal not only means a much heavier weight to support on the brick seatings, but a greater fuel consumption. Assisting the thickness of metal in bringing about the latter drawback is the somewhat poorer heat conductivity of cast iron as compared with wrought iron. Then the uneven thickness of the bottom, at the place just mentioned, combined with the comparatively poor expansive properties and low tensile strength, opens up the risk of cracking. The author has experienced this trouble, which is of a very serious nature. In this connection it should be pointed out that it is practically impossible to repair satisfactorily a cracked cast-iron bottom, and therefore it has to be scrapped—no small matter, as it means the removal of much brickwork before the damaged bottom can be got away and a new one put in its place. Then there is the rebuilding of the brickwork after the repair is finished. It will be noticed on inspecting the diagram (Fig. 20) that flanged joints are used in the building up of the still. This is a most unsuitable kind of joint for a vessel that is subjected to such high temperatures as a tar still. The chief difficulty is to keep the joint tight, even when the faces are perfectly trued up. The risk of a leaky bottom joint is increased somewhat by the fact that the

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[1] See "Corrosion of Industrial Iron Work," by A. R. Warnes and W. S. Davey, *Jour. of Soc. of Chem. Ind.*, June 15th, 1910. The *Gas World*, April 23rd, 1910, p. 528, and May 7th, 1910, p. 599.

[2] See "Coal Tar Distillation," by A. R. Warnes; *Trans. Midland Junior Gas Association* for 1910, pp. 15–29, or the *Gas World*, October 15th, 1910, p. 462.

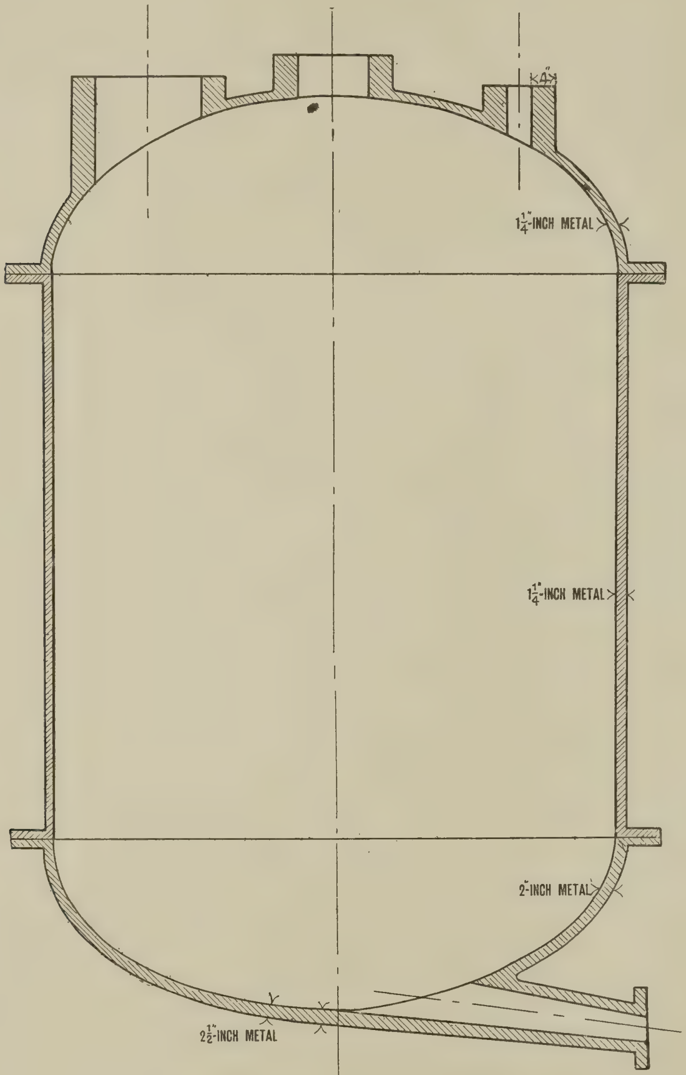

Fig. 20.—Diagram of Cast-iron Tar Still.
(Not to be recommended.)

thickness of the metal of the bottom is greater than that of the sides, thus producing a certain amount of unequal expansion and contraction.

Both mild steel and wrought iron enter largely into the construction of tar stills, but there is a diversity of opinion as to which is the better metal to use. It seems, however, that mild steel is in greater favour. Whichever metal is chosen, it is very necessary to see that the best quality is obtained. In the case of wrought iron there is always the risk of laminations or blisters occurring, even in the best qualities, and the thicker the plates the more liable they are to this defect. The author has frequently seen plates which to all outward appearances seemed perfect open out very badly on shaping, owing to lamination defects. Fracture is frequently caused by laminations or blisters, and corrosion is materially assisted. Owing to the fact that wrought iron is brought into contact with fettling materials (tap cinder, broken slags, red hæmatite) in the course of its manufacture it is not homogeneous in structure, and this state is one which also assists corrosion. Some prefer wrought iron because of its fibrous structure, but this condition must not be considered as an absolute indication of strength. In cases in which shaping has to be done across the grain, there exists the risk of cracking.

Mild steel is, in the author's opinion, the better metal to use. It requires, however, rather more care in working the plates. Well-made mild sheet is perfectly homogeneous in structure, owing to the fact that in the process of manufacture the whole mass is in the state of fusion. There is a greater freedom from impurities, and the tendency to corrode locally is reduced on this account. Mild steel is rather more ductile than wrought iron, and, therefore, is more amenable to the treatment received in the process of cambering, flanging, etc.

Much care is necessary in the process of shaping steel plates, and where possible this should be done by hydraulic pressure. When this cannot be done, and, of course, it is not possible in the case of repairs carried out in a tar distillery, careful attention must be given to the heating of the plates, and in particular to the shaping of them. The plates should be first heated to redness and then beaten into shape with wooden mallets, using cast-iron templet blocks. Metal hammers must not be employed under any circumstances. Research into the causes of corrosion has proved that hammering iron or steel renders it more liable to attack. This is brought about by the production of local strain, and when metal hammers are used this condition is set up to a greater extent than when the plates are shaped with wooden mallets. It has been discovered that overheating renders iron or steel more liable to corrosion, the amount of corrosion product being on an average 20 per cent. more from overheated metal than from metal normally heated.

All rivet holes should be drilled and countersunk on the inside, not punched, thus avoiding the risk of cracking between one hole and another, and also the setting up of local corrosion when the still is in use. A research undertaken by T. Thickens showed that corrosion took place to a greater extent around punched rivet holes than around those which had been drilled, owing to the local shearing strain set up by the punch, and the author has been able to confirm this worker's results. It is as well to bear in mind that carefully punched rivet holes will reduce the strength of a plate about 9 per cent., while in the case of drilled holes the loss in strength is not more than $1\frac{1}{2}$ per cent. Countersinking the rivet holes is also responsible for a small amount of reduction in the strength of a plate, but as the heads of rivets act as points around which "free carbon" collects, and as they retard somewhat the draining away of the pitch, and also hinder the process of cleaning, countersinking is advisable.

It is also policy to use rivets made of the same metal as the plates; and they should be of ample length, to allow a good snap-head to be formed. The seams must be properly caulked, best by machine, as lack of attention to this detail will lead to a number of very troublesome leaks. Machine riveting gives better results than are obtained by hand, and it is also more economical, therefore it should be employed whenever possible. The saving in labour charges is considerable, as for the cost of putting in 100 rivets by hand over 300 can be put in by machine. When rivets are closed by hand there is a liability of them becoming cracked, a condition which is due to the rivet getting too cold before the closing is completed; with machine riveting this is rarely the case. With reference to the diameter of the rivets, and the pitch of the rivet holes, these dimensions should vary according to the thickness of the plate used. A good thickness to employ, at least for the shell, and the one generally adopted (sometimes throughout), is $\frac{1}{2}$ inch. The pitch of the rivet holes and diameter of the rivets should be 2 inches and $\frac{7}{8}$ inch for wrought iron and 2 inches and $\frac{15}{16}$ inch for mild steel. The centre of the rivet hole to the edge of the plate should be $1\frac{5}{16}$ inch for wrought iron and $1\frac{3}{8}$ inch for mild steel. As the top, or dome, of the still is subjected to the action of corrosive vapours to a greater extent than the shell, and with some tars very much more so, it is advisable to construct this portion of the still of slightly thicker plates than those used for the shell. A useful thickness is $\frac{9}{16}$ inch; the pitch of the rivet holes and the diameter of the rivets should be $2\frac{1}{8}$ inches and 1 inch respectively for mild steel and $2\frac{1}{8}$ inches and $\frac{15}{16}$ inch for wrought iron. The centre of the rivet hole to the edge of the plate should be $1\frac{1}{2}$ inches for mild steel and $1\frac{7}{16}$ inches for wrought iron. The author strongly recommends the use of mild steel for the construction of the dome and shell of the still.

It is difficult to say definitely whether wrought iron or mild steel is the best kind of metal to use for constructing the still bottom. The author has had a case in which two still bottoms, one of mild steel, one of wrought iron, and each put into commission at the same time, have "come down" within a week of each other, necessitating the replacing of the greater part of the bottom of both stills. The conditions in this instance were certainly very drastic, the tar being of a very bad quality and the still bottoms not protected in any way by brickwork. The author's experience (bearing in mind the case just mentioned) has caused him to come to the conclusion that, on the whole, wrought iron is the better metal to use. Careful observation has shown that wrought-iron bottoms, properly treated and protected by brickwork when necessary, last longer than those constructed of mild steel. An investigation commenced by the author part of which is not completed, seems to show that metal of fibrous structure is the best kind to use for the construction of still bottoms. In all cases where a still bottom has "come down," cracked, or become badly burned, the metal removed from the damaged parts has been highly crystalline in structure, and very brittle, even when fibrous metal (wrought iron) has been used.

Experiments have shown that this crystalline state takes some time to form in the case of wrought iron ; mild steel is already of a crystalline nature. It appears that the crystalline state is brought about mainly by the iron taking up carbon, and it is quite well known to metallurgists that the greater the carbon content of the metal the more brittle it becomes. Brittleness is a source of weakness in a still bottom in many ways, and the author has known cases in which still bottoms have been cracked, and even pieces knocked out, during the process of still cleaning. A good thickness of wrought-iron plate to use for still bottoms is $\frac{5}{8}$ inch, and for this thickness rivets of 1 inch diameter are necessary. The pitch of the rivet holes should be $2\frac{1}{4}$ inches, and $1\frac{1}{2}$ inches is allowed from the centre of the rivet hole to the edge of the plate.

The author knows of an excellent type of still which is made by the Leeds and Bradford Boiler Co., Ltd. The plates used in building this still are pressed into shape between dies by the use of hydraulic power, the temperature of the plates being kept practically uniform throughout the process. This results in perfectly smooth plates, the metal of which is not fatigued and otherwise damaged, as is the case when shaping is done by the hammer, and the rate of corrosion is thereby lessened ; as has been already pointed out overheating and straining increase the speed of corrosion considerably. All the rivet holes are drilled, *not punched*, and in the case of the bottom plates, these, after shaping, are placed in position and the holes drilled concentrically. This procedure gives a fair hole and does away with incorrect pitching of the holes and the consequent straining of the plates by the abusive employment of the drift. The whole of the riveting, with the exception of one seam of the shell, is done by hydraulic riveting machines and the caulking by pneumatic tools, thus eliminating the risk of cracked rivets and securing thoroughly tight joints.

Tar stills are built in various sizes, the chief being 10, 15, 20, and 30 tons working capacity. The 15-ton size is used very largely in this country, a great point in its favour being that its contents can be worked off in between 14 and 15 hours. Although tar stills of various shapes have been tried from time to time, none of these shapes has proved so satisfactory in use as that known as the pot or vertical still, and it is this type of still that will now be described. The pot still is divided into three chief parts, namely, the shell, which is a vertical cylinder, the diameter of which is a little greater than the height ; the top, cover, or dome, which, in a properly designed still, should have very little rise in it ; and the bottom, which is concave from the outside and pitched high. The still is provided with the following fittings : A safety-valve, or similar contrivance ; a swan neck for conducting away the vapours ; a steam-pipe inlet block, and a steam-pipe inside connected to a perforated coil or criss-cross arrangement ; a charge block, for connecting up to the charging pipe ; a dipping cock, or an overflow cock ; a manlid stool and lid ; and a tail pipe, with cock, for running off the pitch. A thermometer pipe is sometimes fitted either into the dome or the top of the swan neck. The separate parts of the still and the several fittings will now be dealt with *seriatim.*

The shell of the still is built up of wrought iron or, better, mild steel plates, riveted, and of thickness already described. For a 12-ton still the diameter of the shell may be 9 feet 6 inches and the height 8 feet 6 inches ; for a 15-ton still, diameter 10 feet and height 9 feet. The dome, or top, of the still is constructed of sketch plates and a dome plate (see Fig. 21), riveted and of thicknesses previously described. The number of segments or sketch plates varies according to the size of the still or the ideas of the designer ; for instance, in a 12- or 15-ton still this number may be eight. The pitch or rise should not be more than 15 inches for a 12- or 15-ton still. A large number of stills have been and are at present constructed with high-pitched domes ; this is a mistake, as it does not add to the efficient working of the still, nor is it necessary from the point of view of strength, and it materially assists in the process of corrosion. As pointed out by the author in a paper read before the Society of Chemical Industry,[1] corrosion of tar stills is brought about by aqueous vapours containing chiefly ammonium chloride in the dissociated state, and proceeds most rapidly at those points where condensation takes place, and where the condensed vapours are able to trickle down the plates. A high-pitched dome provides all these bad points ; it is more difficult to lag properly, it exposes a greater surface to the cold atmosphere, especially of

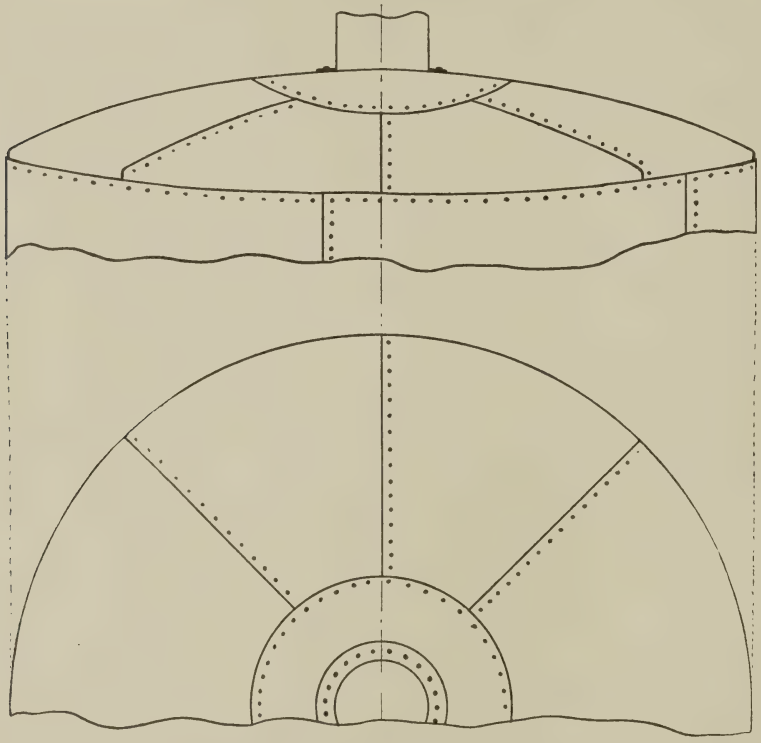

Fig. 21.—Diagram showing a Method of arranging Sketch Plates on Still Dome.

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[1] *Jour. Soc. Chem. Ind.*, June 15th, 1910, No. 11, Vol. 29.

winter (most tar stills are in the open), and the manhole is in a position which further assists in the condensation and temporary retention of the condensed vapours, which eventually trickle down the plate on the underside of the hole. Cases have come under the author's notice in which the plate under the manhole has been corroded through three times in five years, and in all cases of high-pitched domes he has noticed a large amount of grooving on the inside. Fig. 22 illustrates diagrammatically the extent of corrosion which can take place on a high-pitched dome. The correct type of dome to use is shown diagrammatically in Fig. 21.

The process of corrosion of the metal of tar stills is a complicated one, and it is somewhat difficult to form a theory which will fit in with all the conditions that may exist in the still from the commencement to the finish of the tar-distilling operation. In the author's opinion corrosion is due to the dissociation of ammonium chloride, ammonium sulphide, ammonium hydrosulphide, and ammonium cyanide, and the subsequent action of the dissociation products upon the iron. The speed of the reaction is increased, in all probability, by electro-chemical conditions. A state of strain contributes towards corrosion by producing a certain amount of molecular instability in portions of the iron plates composing the still, thus rendering these parts more easy of attack; practical experience has proved this beyond doubt. It is found in practice that still plates are eroded at a greater speed at the parts where excessive condensation takes place, and in all probability this is due, in part, to the continuous flow of liquid removing the final products of corrosion more rapidly at these places than elsewhere, and thus exposing a fresh surface of the iron to the corrosive agents. It is considered that the process of corrosion proceeds at a great rate during the latter portion of the distilling operation and principally during the period when steam is passing into the still, and it is also thought that this steam plays no other part in the process of corrosion than that

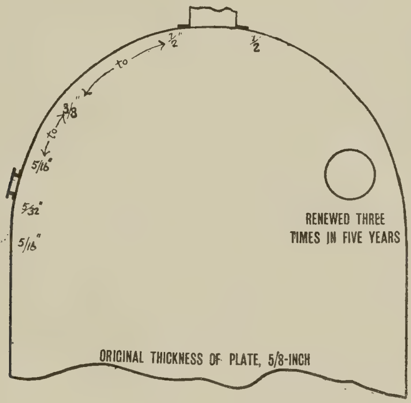

Fig. 22.—Diagrammatic Illustration showing Extent of Corrosion which can take place on a High-pitched Dome.

of producing ionisation of the ammonium chloride, etc., and increasing the power of action of the products of dissociation.

The final products into which the corroded iron is converted appear to be chiefly ferrous sulphide and ammonium ferrocyanide. Ammonium thiocyanate occurs in small quantities, and traces of ferrous chloride and Prussian blue are occasionally present.

The following equations will explain in a more or less simple manner the probable chief reactions which take place in the process of corrosion under consideration :—

1. $NH_4Cl=NH_3+HCl$ dissociation
2. $NH_4HS=NH_3+H_2S$,,
3. $(NH_4)_2S=2NH_3+H_2S$,,
4. $NH_4CN=NH_3+HCN$,,
5. $Fe+2NH_4Cl=FeCl_2+2NH_3+H_2$

$$\left\{\begin{array}{l}2NH_4Cl=2NH_4+2Cl \text{ (ionisation)} \\ Fe+2NH_4+2Cl=FeCl_2+2NH_3+H_2\end{array}\right\}$$

6. $Fe+2HCl=FeCl_2+H_2$
7. $FeCl_2+(NH_4)_2S=FeS+2NH_4Cl$
8. $Fe+H_2S=FeS+H_2$
9. $Fe+2HCN=Fe(CN)_2+H_2$
10. $Fe(CN)_2+\underbrace{4NH_3}\underbrace{+4HCN}=(NH_4)_4Fe(CN)_6$
11. $3CS_2+8NH_3=(NH_4)_2S_3+2NH_4CN+NH_4SCN+2H_2S$

The chief offender in the case of tar still corrosion is undoubtedly ammonium chloride, and this material is in all probability derived from the nitrogen and sodium chloride present in the coal from which tar is obtained. According to Dr. Davidson the amount of sodium chloride in coal varies from 0·05 to 0·25 per cent. L. Crawford[1] examined several kinds of tar for chlorine, and obtained figures varying from 0·0053 to 0·226 per cent.

The still bottom should be constructed of wrought-iron plates, of a thickness already described, and these plates must be well riveted and properly caulked. Sometimes still bottoms are constructed in one piece, but this is not a good plan ; it makes repairs more costly and the bottom is not so strong. The most satisfactory way is to construct the bottom of a number of segments, or sketch plates, united at the crown by a circular plate known as the crown-plate. The number of segments may vary between 8 and 12. Methods of arranging these and the crown-plate are shown diagrammatically in Figs. 23 and 24. The diameter of the crown-plate varies between 2 feet 6 inches and 3 feet. It is advisable that the rise or pitch of a still bottom should be as great as possible. For a 12- or 15-ton still the rise may be 2 feet 9 inches, and for a 30-ton still 3 feet 6 inches. The bottom is joined up to the shell in two ways : (*a*) by angle iron, and (*b*) by means of what are known as channel plates. The latter method is the better. Figs. 25 and 26 show diagrammatically the two methods. Important points to bear in mind when constructing still bottoms are the necessity of securing as complete a draining off of the pitch as possible, and to avoid the introduction of joints which increase the tendency of the pitch to lodge and ultimately coke. Joints which make the work of still cleaning difficult should also be avoided. The angle-iron joint possesses the defects just mentioned, the nearness of the rivets acting as a nucleus for deposits which eventually coke (see Fig. 25). If channel plates are used, however, the risk of these troubles occurring is much minimised, and one of the best types of channel plate to adopt is shown in Fig. 26. It is not advisable to make butt joints when connecting up the channel plates; lap joints are the best.

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[1] *Gas World*, Coking Section, May 4th, 1918.

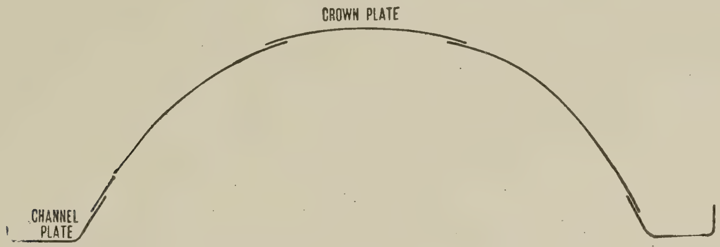

Fig. 23.—A Method of arranging Plates for Still Bottom (Diagrammatic).

The advantages of building a high-pitched bottom to a still are, (*a*) a large heating surface is secured, (*b*) the metal can contract and expand with comparative ease, thus minimising strain, (*c*) the stiffness of the bottom is increased, (*d*) the draining off of the pitch is materially assisted.

When a tar still is working normally there should be very little pressure inside, but should a stoppage occur in any portion of the condensing worm, a serious pressure may be set up. In order to give warning that a stoppage has occurred, and at the same time relieve abnormal pressure, a safety-valve, or a similar contrivance, must be fitted to the still. Safety-valves of the dead-weight type are the best to use. The valve should be designed with as shallow a casting as possible on the vapour side of the seat in order to avoid a stoppage by solidified anthracene or naphthalene salts. A type of valve designed by H. Astbury and the author, which in practice has given excellent results, is shown in Fig. 27. The safety-valve stool should be

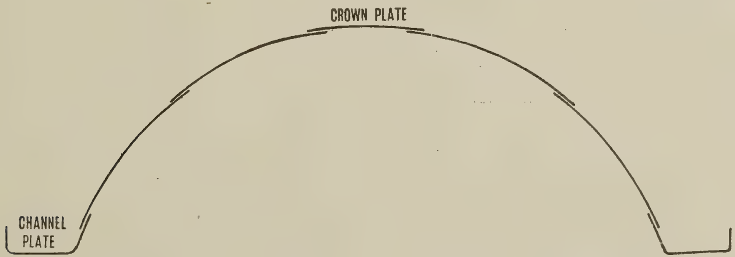

Fig. 24.—A Method of arranging Plates for Still Bottom (Diagrammatic).

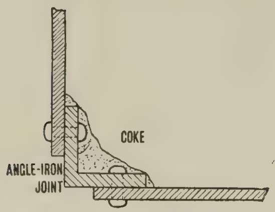

FIG. 25.—ANGLE METHOD OF JOINING BOTTOM OF STILL TO SHELL.

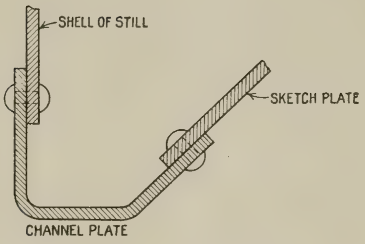

FIG. 26.—CHANNEL PLATE METHOD OF JOINING BOTTOM OF STILL TO SHELL.

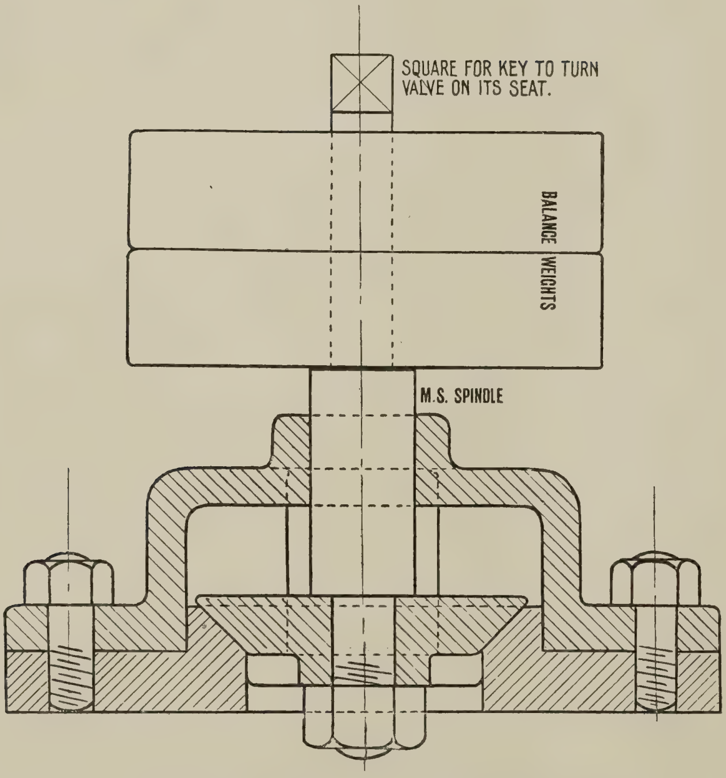

FIG. 27.—A TYPE OF TAR STILL SAFETY-VALVE.

cast as shallow as possible, and riveted on to the still dome (see Fig. 28). The seat should not be too narrow, and the valve should be weighted to blow off at a pressure of 6 lbs. to the square inch. Another contrivance, often known as the S-pipe, is illustrated in Fig. 29. This device is nothing more than a water seal, the two limbs of the U-bend being filled with ordinary water. The length of each limb should be 3 feet 9 inches and the internal diameter of the tube $\frac{3}{4}$ or 1 inch. There is a much greater risk of this safety contrivance becoming clogged than with the safety-valve just described; the clogging generally occurs in the upright tube which is connected to the still. The S-tube may be fitted to the top of the swan neck, or on the still dome.

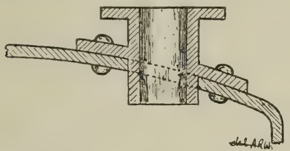

FIG. 28.—SAFETY-VALVE STOOL.

The risk of fire when a safety-valve blows off is well known to all those who have had charge of a tar distillery, and in order to minimise this danger enclosed safety-valves have been designed and recommended. From one side of the casing which encloses the valve a pipe is led off which is intended to carry the vapours as they escape from the safety-valve to a coil in which they may be condensed. Some enclosed valves are fitted with an electrical contact, so that when the valve seat lifts contact is made and a suitable signalling apparatus is brought into action by which the workman is warned of the danger.

In the opinion of the author the use of enclosed safety-valves is a somewhat risky one, as, should the still be working, say, tar of a high naphthalene content, or should the process be near the finish, and the safety-valve blow, then in the former case vapour of high naphthalene content and in the latter pitch vapour, will leave the valve, and there is a great risk of the pipe leading from the valve becoming choked. If this occurs then the object of the safety-valve is defeated. It is far better to attend to the design of the fireplace so that the vapours cannot easily reach the fire, and leave the safety-valve open to the atmosphere.

The swan neck should be made of cast iron, and is bolted on to a swan-neck stool (see Fig. 30). Cast iron is used because it is easier to manufacture a fitting of this shape in that metal, and it also resists to a far greater extent than wrought iron or mild steel the corrosive action of some of the tar distillates.

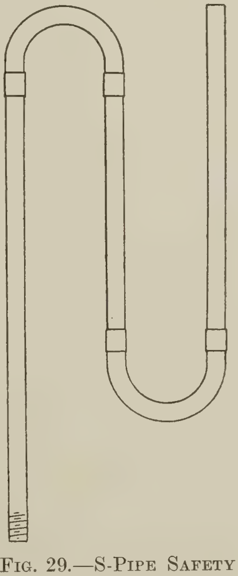

FIG. 29.—S-PIPE SAFETY CONTRIVANCE: USED INSTEAD OF A SAFETY-VALVE.

In the making of these castings it is not wise to employ chaplets, as at their points of introduction local corrosion is almost sure to take place, due to electrolytic action set up by the difference in potential between the chaplet metal and that of the casting in the presence of moisture containing ionised ammonium chloride.

The internal diameter of the stool should be 12 inches and the swan neck tapers from 12 inches down to 4 inches. A flange must be cast on the narrow end for the purpose of attaching it to the condensing coil. The swan-neck stool should have cast on to it a short length of about 4 inches beyond the lower flange, which will project into the still when the stool is riveted into position. This will prevent any condensed vapours from trickling down inside of the dome, and so assist in minimising the rate of corrosion of the plates of the dome.

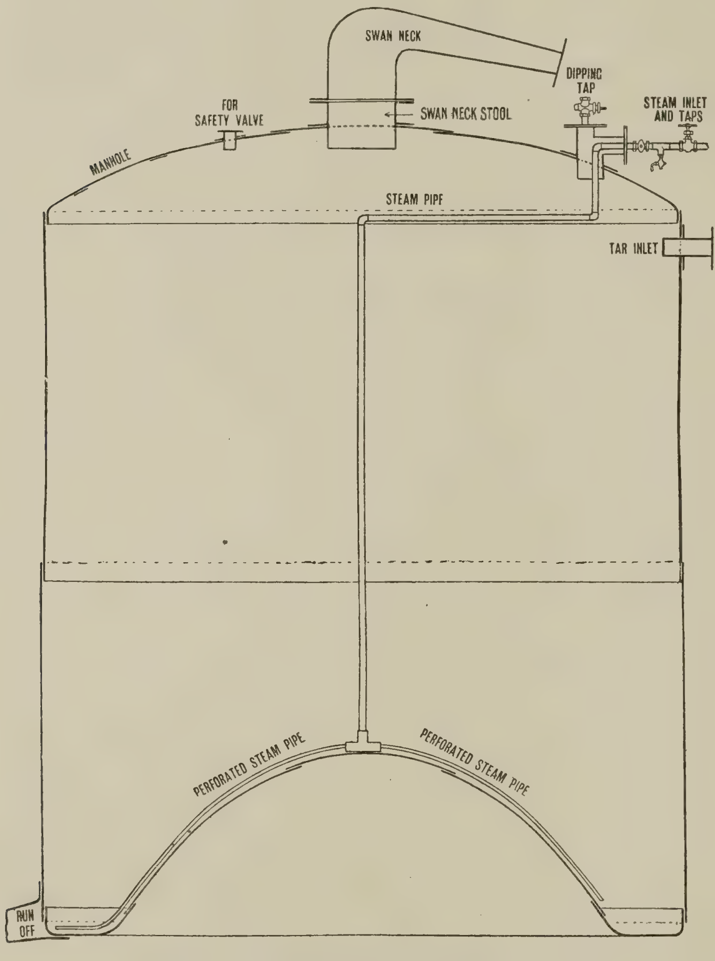

FIG. 30.—DIAGRAMMATIC ILLUSTRATION OF TAR STILL.

For the purpose of reducing the temperature towards the end of the tar-distilling operation, and to keep the still contents in a state of agitation, in order to prevent as far as possible the coking of the pitch on the bottom plates, it is usual to provide the still with open steam coils. At the point where steam enters the still, it is necessary to fit a steam-pipe inlet-block, which is made of cast iron, and of a design shown in Fig. 30. It is just as well to provide two valves on the steam main in order to reduce the risk of a leakage of steam or condensed steam into the still, should one valve become defective (see Fig. 30), and it is not a bad plan to introduce a small pet cock between the two valves, through which any water may be blown before steam is admitted into the still. Fig. 30 illustrates this. The steam inlet pipe may be of 1 inch or 1¼ inch internal diameter, and this pipe is connected inside the still to one of a similar diameter, and of such a length that it reaches the crown plate of the still bottom. Here it is coupled up to a 4-, 6-, or 8-way piece. Into the outlets of these fittings, pieces of perforated pipe, bent to conform to the shape of the still bottom, are fitted. The internal diameter of these pipes should be about ½ inch, and the holes are best drilled in such a position that the steam, as it emerges, impinges upon the plates of the still bottom. A satisfactory pitch for the holes is 6 inches, and it is advantageous to drill them on each side alternately, an occasional one being placed right underneath. The end of each steam-pipe should, of course, be closed by a plug or cap. As regards the lengths of the perforated pipes these often have to be determined by a working experience with the still into which

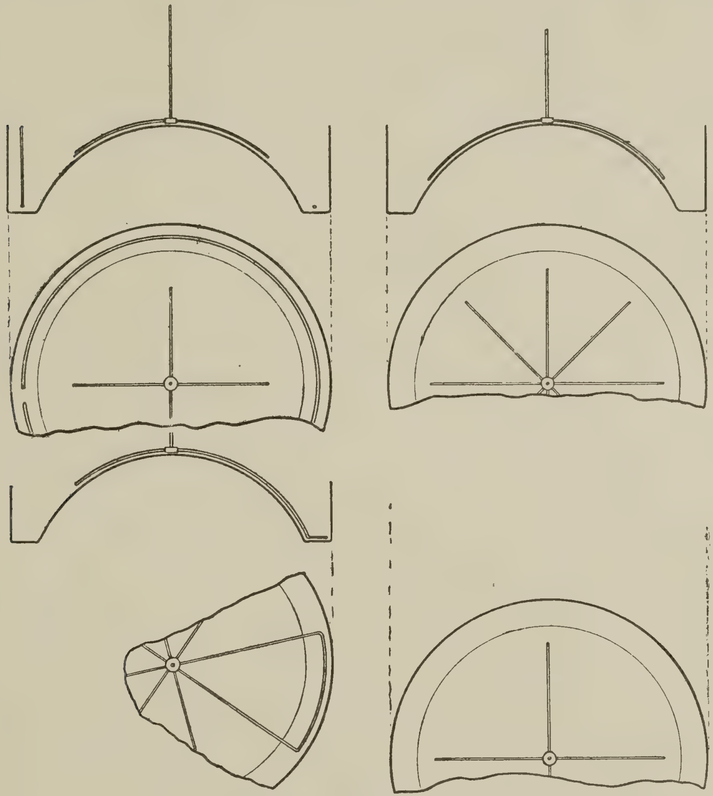

FIG. 31.—ARRANGEMENT OF STEAM-PIPES.

they are put. It is often found that coking will take place to a greater extent on one part of a still bottom than another, and sometimes even in the trough or channel, and when this occurs it is necessary to arrange that jets of steam play upon these parts. Several methods of arranging these pipes are shown diagrammatically in Fig. 31.

To couple up the charge pipe to the still, a casting often termed a charge block is provided. This fitting is riveted on to the still, either just below the point from which the still top or dome springs, or just above that point on the dome itself. Of the two positions the latter is the better, in any case so far as minimising corrosion is concerned. In the author's experience, with inlets fitted to the still side there has always been serious corrosion. A good type of charge block and two methods of fitting it to the still are shown in Fig. 32.

In order to prevent overcharging, the still should be fitted with a dipping cock or an overflow tap. The latter is preferred by some; and if it is desired to fit it to the still, it should be placed at the full-charge level. An arrangement for carrying away any tar which may overflow must be provided. If the still is charged from a preheater, or a blow-boiler which contains an exact still charge, then an overflow tap is not necessary. It is contended by some that a dipping tap is unnecessary; but particularly in the case of stills charged by preheaters, it is advisable to use this fitting, as there is a possible chance of the charge pipe between the preheater and the still becoming stopped, and the use of the dipping tap provides a ready means by which the stillman can find out that the still is charged and also approximately check the volume of tar in the still. The dipping tap may be an ordinary 1-inch cast-iron plug cock, and it is advisable to rivet it to the still by means of a flange. A combined steam inlet and dipping tap block is shown in Fig. 30. The dipping rod can be made of narrow flat bar iron. For an overflow cock some prefer to use a 1-inch brass or gun-metal bib-cock, but as these metals are so easily corroded by sulphuretted hydrogen, ammonium chloride, etc., it is, in the author's opinion, best to use cast-iron gland cocks for this purpose.

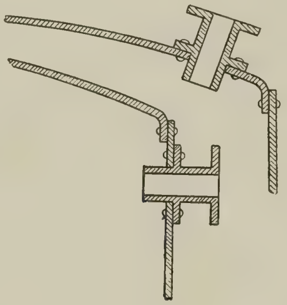

FIG. 32.—DIAGRAM SHOWING METHODS OF FITTING CHARGE BLOCKS TO STILL.

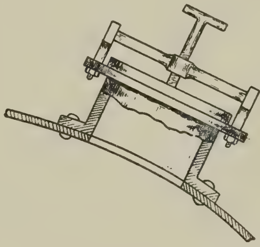

FIG. 33.—MANHOLE AND LID, WRONG TYPE.

In order that men may enter the still for cleaning purposes, conducting repairs and making inspections, it is necessary to provide the still with a manhole and a lid to cover it. As there is an element of danger to the workman while he is inside the still, it is advisable to make the manhole rather larger than the regulation size employed by boilermakers. The reason for this is that should a man become "gassed" and have to be hauled out of the still at the end of a rope, great difficulty would be experienced in dragging the man through a regulation size manhole, and in cases like this rapidity of action is of the utmost importance. Oval manholes of 18 inches by 12 inches could be used with advantage.

It is a common practice to construct manholes as shown in Fig. 33. This is an expensive and also unsatisfactory design. Owing to the large amount of surface exposed to the cooling influence of the atmosphere, excessive condensation takes place in the casting, and the condensed vapours trickle down the side of the still. This brings about excessive corrosion. There are cases which have come under the author's notice of still plates having an original thickness of $\frac{5}{8}$ inch being corroded through in eighteen months. The best type of manhole and lid to employ is shown in Fig. 34. This design enables the stillman to cover the manlid completely with lagging; for instance, a silicate cotton mat, after he has drawn the manlid tight. There are no projecting surfaces, and even if lagging is not used, the risk of condensation is very much less than if the type shown in Fig. 33 is adopted.

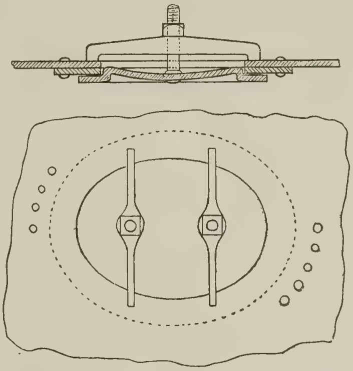

Fig. 34.—Draw-up Manlid, Correct Type.

The tail-pipe or run-off pipe should be constructed of wrought iron or mild steel, and should be riveted to the still casing and channel plate. One example of how this is done is shown in Fig. 30. The portion attached to the still must be carefully flanged, and the rivet holes drilled, *not punched.* It may be 4 inches or 6 inches in diameter, and not less than 18 inches long, and should be provided with a flange, welded on, in order to connect it with the run-off cock. The run-off tap may be of the main cock or Butterfield type (Fig. 35), and the plug should have a full-way. In the experience of the author cast-iron gland cocks do not give such satisfactory results. It is advisable to place an expansion joint between the cock and the pipe which connects it to the pitch cooler.

In this country a thermometer is not often fitted to a tar still, in spite of the advantages it offers, but if it is desired to use one then it is advisable to enclose it in a case or tube. This tube may be constructed of wrought iron, welded at the bottom, and a few holes drilled at that point; cast iron is, perhaps, a better metal to use for the tube from the point of view of corrosion. The top portion is provided with a flange by means of which it is riveted to the still dome, and it should be placed as near the swan-neck stool as possible. To the thermometer is fitted a threaded collar so that it can be screwed into the tube and thus prevent the escape of vapours.

To fit both the still and the combustion chamber of the furnace with distance or recording thermometers is useful from the point of view of gaining knowledge as well as to keep complete control of the distillation process. The Negretti and Zambra patent transmitting thermometer, a very reliable and sensitive instrument the error in the reading as a rule not being more than 0·25 per cent., can be fitted to a tar still and the dial placed in a position level with the stillman's eyes, thus doing away with the need of mounting to the still top to ascertain the temperature of its contents during distillation, and minimising the risk of accident especially on the night shifts, and also facilitating matters in connection with changing over from one fraction to another. If it is desired to record temperature against time then a thermograph or recording transmitting thermometer may be used in the place of a dial thermometer. As a matter of fact this instrument can be read by the stillman quite easily, and on this account will serve the dual purpose of indicating change-over points and keeping a permanent record of the temperature—time of an operation.

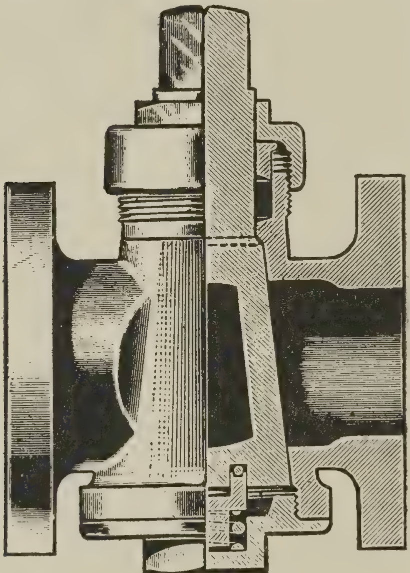

Fig. 35.—Butterfield Cock.

In addition to distance thermometers (dial and recording) the Cambridge and Paul Instrument Co., Ltd., manufacture a useful electrical distance indicator which can be connected to a number of thermometers and by the manipulation of a switch or " plug " a reading can be taken of the temperature, for example, of a still furnace or its contents. It is possible for two or three stills to be connected to one indicator.

CHAPTER VII

PLANT USED IN THE DISTILLATION OF TAR *(continued)*

It is important that tar still foundations be good solid ones, and as the nature and bearing strength of soils vary, thus influencing the method of construction, it is wise, before erecting a single tar still or a battery of them to give careful consideration to the choice of the site. The soils (or rather what lies below the soil and sub-soil) usually met with in practice are sand, gravel, clay, chalk, and the harder types of rock. If not already known, the condition of the site should be examined, and if it is found to consist of spongy soft gravel, peat, quicksand, sand liable to be affected by running water, soft wet clay or marsh clay, then the position should be rejected. Firm sand, compact gravel, solid clay, indurated marl, hard chalk, limestone, sandstone, or other kinds of rock are the best to build upon. In the cases of the four first-mentioned materials (firm sand, etc.) it is a very wise procedure to put in a foundation of properly prepared cement concrete of a thickness varying between 6 inches and 9 inches according to existing conditions, but if the stills are to be erected on chalk, limestone, etc., then any unsound portions must be cut away, and the gaps filled in, and the site levelled up with cement concrete. It should be borne in mind that in cases of foundation building it is as well to err on the side of safety, and should there be any doubts as to the state of the natural foundation, a thicker concrete foundation, or one made of reinforced concrete, should be put in. Although cheaper, lime concrete must never be used, and cement which has become damp should be studiously avoided for concrete making. Due regard must be paid to the time taken for cement concrete to set: if, after a lapse of twenty-four hours, it is found to be soft, the lot should be pulled out and replaced by a better make. For further particulars on concrete the reader is referred to pages 112–116. Every endeavour should be made to avoid excessive settling of a tar still, for if this takes place many difficulties will subsequently arise. The making of a satisfactory joint between the swan neck and the condenser coil will not be possible; the incomplete draining away of the pitch from the still, and serious cracking of the flues, are some of the troubles which will be brought about.

To a very large extent the efficient working of a tar still depends upon the care used in the designing and building of the flues and the setting of the still. Bad designing and careless building will result in one, several, or all of the following troubles: (*a*) An excessive consumption of fuel; (*b*) a prolonged operation, resulting in extra labour, expense, etc.; (*c*) boiling over at the commencement of the operation; (*d*) burning of the still shell; (*e*) increased corrosion, owing to unequal heating producing strain or to severe heating of plates not covered with liquid; (*f*) bringing down or burning out of the still bottom. As much attention should be paid to fuel economy in connection with tar stills as with steam boilers. It is quite possible in a large works to burn per annum 600 tons of coal over and above the normal quantity, should the flues be improperly built. This is no small item.

The flues and the fireplace should be constructed of the very best firebrick and fireclay; easily fused firebrick will cause no end of trouble if used, therefore bricks having a melting-point or fusing-point above 3000° F. are the best to employ. They must be free from holes or flaws, and should not show more than 1 per cent. of linear contraction or expansion when submitted to a temperature of 2500° F. For outside work, a non-absorbent brick must be used, and brindled or Staffordshire blue bricks prove very satisfactory in this case. The object of using this type of brick is to prevent the absorption of moisture during rainy weather, for if this takes place, serious cracking of the brickwork will inevitably follow. In a battery of stills the spaces between the outside of the flues and the straight edge of the outer wall (see Fig. 36) should never be filled in with grouted broken brick or concrete, but should be built in properly with common brick set in ordinary mortar. The mortar should not be laid too thickly between the bricks, either for the inside or outside work: a thickness of $\frac{3}{16}$ inch is ample. This remark applies also to the fireclay used in setting the firebricks. The firebricks must be clean and free from dust before laying, and if very dry they should be well wetted with water, otherwise the fireclay will not adhere properly to them. The author recommends pointing the outside work with neat cement, and covering that at the top with cement rendering roughed with coarse grit. The object of roughing is to minimise the risk of the stillman and his assistants slipping when walking on the still top. It is advisable to build the top brickwork with a slight fall towards the edge and to put in an overhanging coping of round or bull-nose bricks (see Fig. 37).

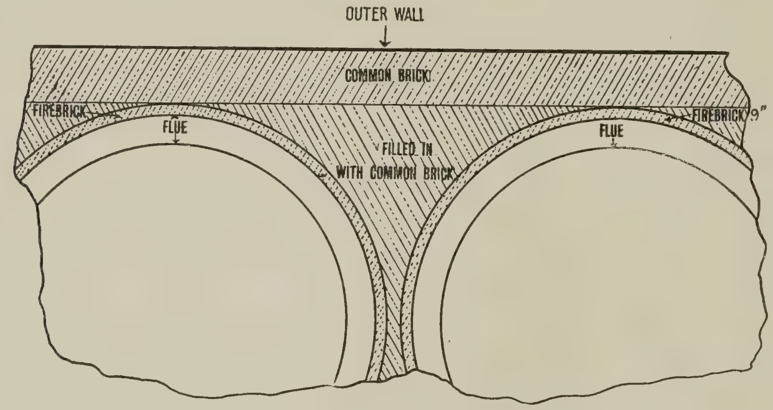

Fig. 36.—Showing Method of Filling in between Stills and Outer Walls.

The thickness of the ordinary brickwork outside the flue should be at least

18 inches. In the case of a single still, this brickwork may be built round the flues, forming a cylinder. It is necessary to strengthen the brickwork by encircling it with straps or bands made of flat bar iron. The brickwork of a battery of two or more stills will remain in excellent condition, and not develop serious cracks, etc., if strengthened by means of buckstaves and tie-bars.

The structure from the concrete foundation to the under portion of the floor of the combustion chamber is built of ordinary brick. It is necessary, however, to build the floor of the combustion chamber with firebrick. This kind of brick is also used to build the still seating, and, of course, the flues. In the lower portion of the structure an opening is left for the ash-pit, the floor of which should be, for preference, on a level with the ground. Some tar distillers prefer to build the ash-pit below ground, but in the author's opinion this method is not so safe as the former, should the still bottom spring a leak, and the ignited tar commence to run rapidly into the ash-pit. It is much easier to put out a fire with sand in the case of an ash-pit built on the floor level than one built below ground. The fire-bars are of that pattern employed for burning small coal (slack or smudge), and are supported on bearing bars and provided with a dead plate, as usual. A cast-iron door frame is

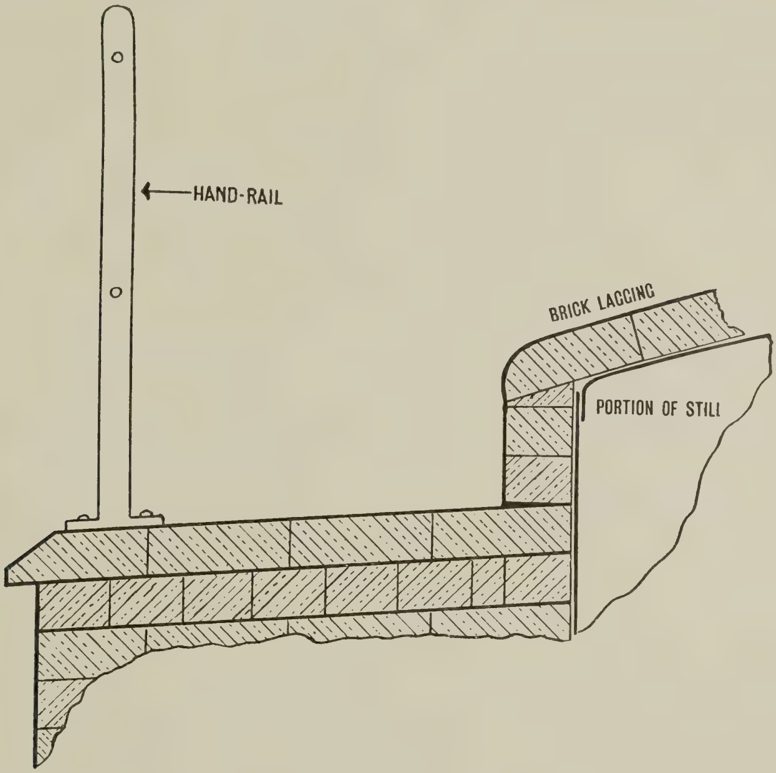

Fig. 37.—Brickwork of Still Top with Coping.

built in and arched over during the building of the front portion of the external brickwork.

The still is supported on an annular ring of firebrick, 9 inches in width, built several courses high, and sprung from the floor of the combustion chamber (see Fig. 38). At a point opposite the fire-door position, openings are left for the purpose of allowing the passage of flame and hot gases to the flues. The portions of the channel plate of the still over these openings in the annular ring must be very carefully protected by building small brick arches under them (see Fig. 40), otherwise the metal will soon suffer severely. With reference to the size of these openings, they will vary according to the dimensions of the still, one 9 inches from the base to the top of the arch rise by 1 foot 6 inches wide will prove large enough for most purposes. In between the top of the arch rise and the channel plate of the still at least 12 inches of firebrick should be built. If preferred openings can be left in the annular ring and these covered with firebrick slabs of at least 3 inches in thickness, but in the case of stills which are to be used for working tars liable to deposit much free carbon, then it is wise to protect the portions of the channel plate over these openings (or pigeon-holes) by using four of these slabs, making a thickness of 12 inches between the channel plate and the flames and hot gases.

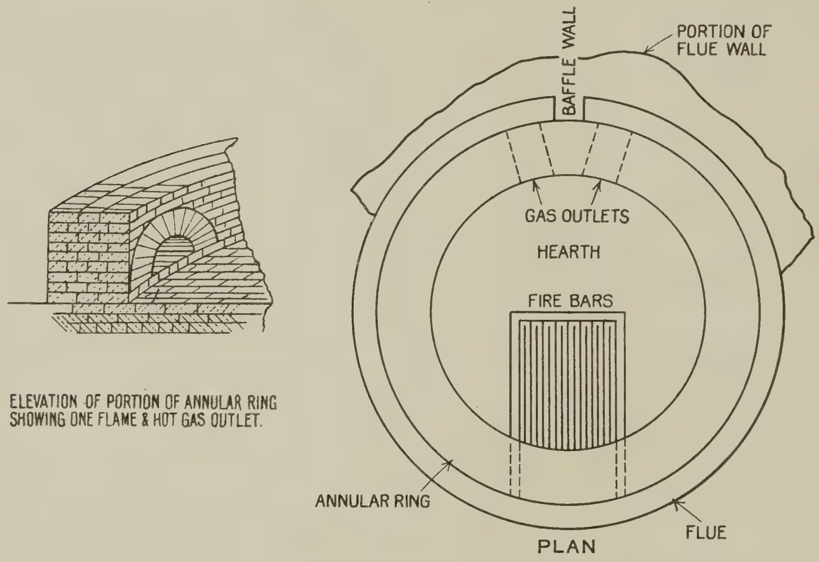

Fig. 38.—Annular Ring (Still Seat) Outlets to Flues.

It is advisable in most cases to protect the bottom of the still with a firebrick arch, known technically as a curtain arch. This arch is sprung from the annular ring just referred to (see Fig. 40), and is constructed of the best quality of firebrick. It should be built in such a fashion that it provides approximately 4½ inches of brickwork against the still bottom. Some tar distillers prefer to leave a small air space between the firebrick and the still bottom; the writer can recommend this method in cases of bad tar.

It is contended by certain workers that the burning and coming down of tar still bottoms is due almost entirely to faulty design. With this the author cannot altogether agree, as in his experience properly designed stills set in correctly built flues have given a very great deal of trouble in connection with the bottoms, the cause being "bad" tar (*e.g.* a tar of high specific gravity containing a large percentage of "free carbon"). Unprotected still bottoms can be used advantageously with "good" tars, and there is a saving in fuel consumption, coupled with a little more ease in the matter of control of the rate of distillation, but it must be kept in mind than any saving in fuel may be quite easily negatived by extra costs for repairs to bottoms and pulling down and replacing brickwork, in addition to the inconvenience caused by the still remaining idle, should the tar happen to be of the "bad" type. In connection with this matter the following figures may be of interest to students and other readers: Mean of 20 workings of a still with unprotected bottom, 1·17 cwts. coal per ton of tar distilled; highest 1·22 cwts., per ton of tar; lowest 1·10 cwts. per ton of tar. Mean of 20 workings of a still with protected bottom, 1·41 cwts. coal per ton of tar distilled; highest 1·46 cwts. per ton of tar; lowest 1·38 cwts. per ton of tar. In another case the extra amount of coal used under stills with protected bottoms for a period of twelve months cost £92, while the saving in repairs to the bottoms amounted to £111.

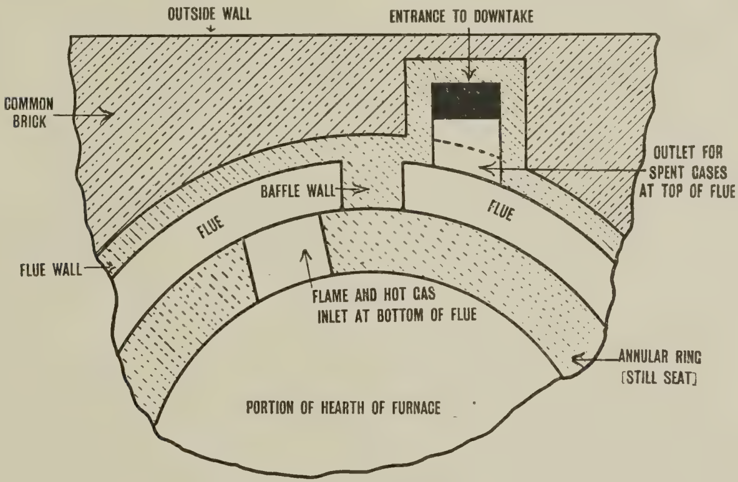
OUTSIDE WALL
ENTRANCE TO DOWNTAKE
COMMON BRICK
OUTLET FOR SPENT GASES AT TOP OF FLUE
BAFFLE WALL
FLUE
FLUE
FLUE WALL
FLAME AND HOT GAS INLET AT BOTTOM OF FLUE
ANNULAR RING [STILL SEAT]
PORTION OF HEARTH OF FURNACE

FIG. 39.—DIAGRAMMATIC REPRESENTATION OF GAS INLET AND OUTLET IN SINGLE WHEEL FLUE (plan).

In order that the pitch can be run off readily and the still drain well it is necessary to place the still on its seat with a fall towards the tail or run-off pipe. This may be approximately ½ inch to the foot, or, say, for a still of 9 feet 6 inches in diameter, 4½ inches. The run-off pipe and cock are liable to become "set-up" with a plug of cold pitch at times, especially during cold weather, and to avoid this trouble as much as possible this appendage to the still must be protected from draughts and cold air. This is done by building in the greater part of the tail pipe and constructing a brickwork recess to cover the run-off cock. Into the recess, and covering the cock, a quantity of sand is placed before commencing the distillation. Should by any unlucky chance the cock become "set-up," then a little cotton waste saturated with creosote can be placed under it and ignited, and the heat from the combustion will melt the pitch and set the plug of the cock free.

Of the several types of flue, that known as the wheel flue is the best. This kind of flue is built single or double according to the size of the still: a single flue being used for small stills up to 15 tons, and double flues for the larger sizes. In the case of double flues two openings must be built in the still seat instead of one, in order to split the hot gases and send them in opposite directions round the bottom of the flue. These openings need not be quite so large as that of the hot gas exit of a single wheel flue. Immediately above the arch over the firebars a 9-inch mid-feather or baffle wall is built to the total height of the two flues. On each side of this mid-feather an opening is made in the lower flue cover, in order to allow the hot gases to pass into the upper flue, the mid-feather causing the gases to flow in two directions towards the back of the still, where they come to the downtakes, which in turn lead to the main flue. A damper is always fitted in the downtake to regulate the supply of air and control the combustion of the fuel. The top flue is covered in by corbelling several courses of firebrick, or using firebrick flue covers, *i.e.*

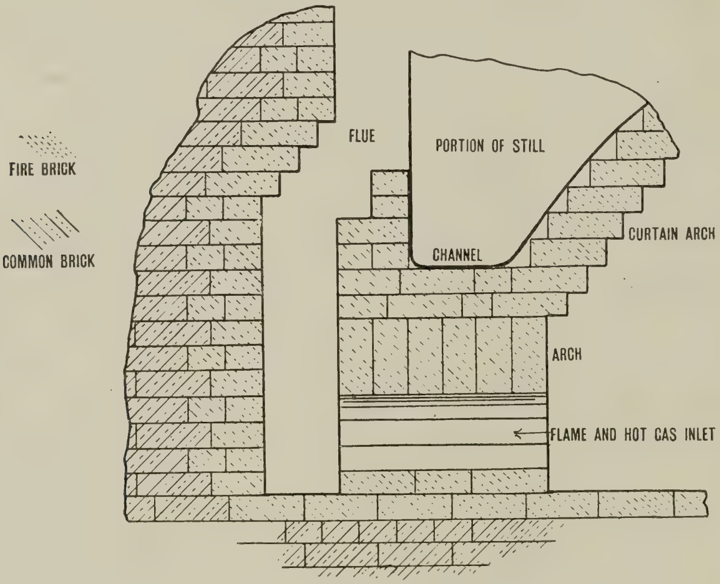

FIG. 40.—DIAGRAM SHOWING ONE METHOD OF PROTECTING BOTTOM OF STILL SHELL, ALSO CHANNEL PLATE AND BOTTOM.

slabs of firebrick known as burrs. The under side of the flue cover must be at least 9 inches below the level of the residual pitch at the finish of the distillation, in order to prevent overheating of the plates of the still shell. Tar still flues are generally built 9 inches or 12 inches wide, and of a depth varying with the size of still.

In a single wheel flue the mid-feather or baffle wall must be built in between the gas inlet to the flues and the downtake, in order to cause the hot gases to encircle the still completely (see Fig. 39). The width of the flue may be the same as that of the double wheel flue, and it is covered in in a similar manner. Whether double or single wheel flues are built, it is advisable to protect the bottom portion of the still shell with a few courses of firebrick when very bad tar has to be distilled. In order that this may be done it is necessary to recess the outer bottom portion of the flue. Fig. 40 illustrates the manner in which this is carried out. To secure the most satisfactory result the firebrick lining of the flues should be built of circle bricks of the required radius. These can be made to order, and may be obtained from any responsible firebrick manufacturer.

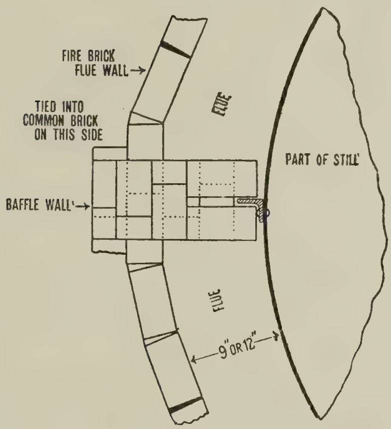

Fig. 41.—Diagram showing a Method of keeping Flue Tight at Baffle Wall.

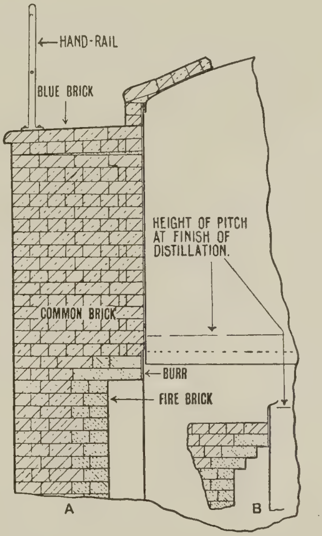

Fig. 42.—Two Methods of covering in Flues: A, with Firebrick Burr; B, by Corbelling.

In building the flue, it should be remembered that the still shell will expand and contract throughout each operation. There is on this account always a certain amount of difficulty in keeping the various parts of the flue tight. In the case of the mid-feathers or baffle walls this may be overcome almost completely by riveting a piece of angle iron to the still, and building the firebrick on both sides of the projecting portion, as shown in Fig. 41. As regards the top cover of the flue, there is less difficulty here, owing to the number of courses of brick built above it, and the manner in which the top of the still is covered (see Fig. 42). As the flues are liable to become partly choked with dust after a period of working, especially if solid fuel is employed, air-tight dust-doors fitted in convenient positions will be found useful for cleaning purposes. Only skilled furnace builders should be employed to erect the furnaces and flues ; ordinary bricklayers, as a rule, are not sufficiently conversant with this kind of work, and will generally turn out an unsatisfactory job.

If it is desired to employ gas for firing, careful attention must be given to the design and building of the gas and air inlets, passages and burner. Ignition of the gas should not take place until it has reached the combustion chamber, and the air and gas should mix just before they enter that place. The volume of air and gas is controlled by valves, slides, or dampers, and the gas is admitted to the burner passage from the gas sewer, conduit, or main gas flue by a mushroom valve, controlled by a spindle and wheel. Both the gas and air passages are built of firebrick throughout, and, of course, will run parallel to each other. Water-air gas is generally forced into the gas sewer from the producer, and is therefore hot when it reaches the gas-burner. The air is warmed a little during its passage to the burner end by the hot bricks with which it comes in contact. Two methods of building a producer gas burner are shown in Fig. 43. The ordinary firegrate is not dispensed with : it is useful in case the gas supply fails, and sometimes as an auxiliary. If desired, a Terbeck or Cumberland burner may be employed instead of using the burners just described. Figs. 44 and 45 will give a general idea of these pieces of apparatus. The firing of tar stills is dealt with on pages 145 and 147.

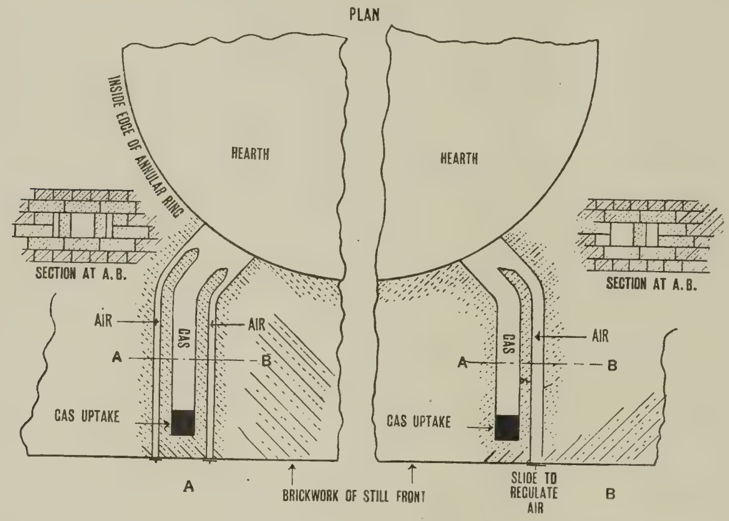

Fig. 43.—Diagrams A and B showing, in Plan, Two Methods of building a Producer Gas Burner of Brick.

After the still settings are finished sufficient time should be allowed for the brickwork to dry out. If "green" brickwork is heated a quantity of steam is generated and this, due to expansive force, brings about cracking, sometimes of a serious nature, which will eventually lead to a weakened structure and leaky flues. It is wise to allow one or two months to elapse, according to existing conditions, before starting up the fire, the damper being kept open all the time in order that a current of air can pass through the flues and assist in drying the brickwork. A few days before starting the still it should be charged with tar and a slow fire lighted in the grate and kept going for two or three days.

The gas sewer or conduit is built below ground, along the whole range of stills, and careful brick setting is necessary in order to avoid leakage of gas. The outside brickwork should be of best blue brick, and the joints made of cement mortar, and not too thick. The lining is built of firebrick, properly tied into the outer wall. The conduit is covered in with a semicircular arch of firebrick internally, and blue brick externally. It is advisable to provide the conduit with several inspection holes about 18 inches by 2 feet 6 inches in size, covered with cast-iron lids.

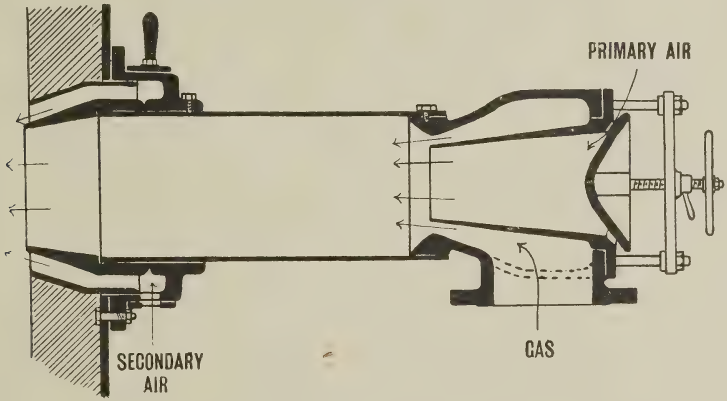

Fig. 44.—Mixing Tube of Terbeck Gas-fired Furnace.

Several advantages are secured by the use of producer gas for firing tar stills, among which may be mentioned : (*a*) The operation of distillation may be controlled somewhat more easily ; (*b*) the risk of prosecution for making black smoke is obviated ; and (*c*) fewer men are required to work a battery of stills. A little more coal is burned per ton of tar if producer gas is the fuel employed, but the cost of this is not so great as that for extra labour if the furnaces are coal fired. For instance, an experiment made on a battery of tar stills run twenty times on coal fires and twenty times on gas fires, using producer nuts as the fuel in both cases, gave the following average results : With gas firing consumed 1·32 cwts. coal per ton of tar distilled, and with coal firing 1·16 cwts. coal per ton of tar distilled. The extra cost for coal when using producer gas approximated 0·48d. per ton of tar distilled, while the extra cost for labour when the furnaces were coal fired approximated 0·84d. per ton of tar distilled.

It is convenient in this place to say a few words on the subject of still firing. As with steam boilers, the firing of tar stills should receive strict attention in regard to fuel economy. It is an easy matter to secure poor efficiency with either coal or gas firing, even if the still settings are of the first order, if the still fireman is careless in the way in which he manipulates his coal fire or his gas-burner.

In the case of coal firing many firemen are devoted to what is known as " spreading firing " or " spreading," as this method gives them the least trouble, but it should not be allowed owing to the fact that it is uneconomical and black-smoke-producing. If the practice of firing little and often is coupled with " spreading," and if due care is taken to admit the correct quantity of air, the production of black smoke is much reduced, but as this method means hard work it is not likely to receive favour at the hands of the ordinary still fireman.

Another variety of firing known as " ribbon firing " is a modification of " spreading firing " and it consists in throwing the " green " or raw coal over one half of the grate, from front to back, allowing this to become partly consumed and then carrying out the same procedure on the other half of the grate. Owing to the fact that the amount of gas set free from the coal at each firing operation is much less than in the " spreading " method, the mixing with air and raising to the required temperature for combustion is facilitated, and this system can be considered as an improvement on the one just mentioned.

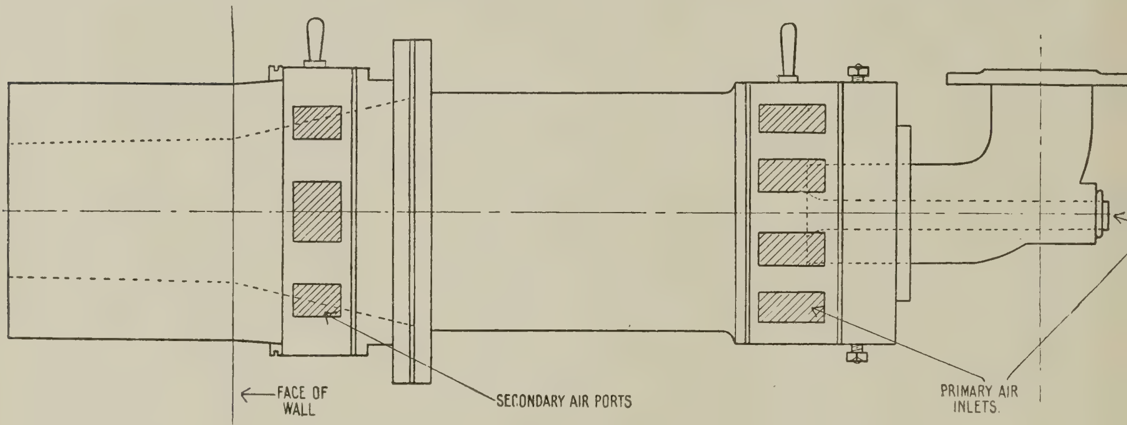

Fig. 45.—Cumberland Patent Standard Producer Gas-burner.

The best method of firing is known as " coking firing," and it consists in shovelling the coal on to the dead plate and front ends of the firebars. As the fuel becomes incandescent it is pushed towards the back of the grate and more " green " coal supplied to the front. With this method, there is little, if any, black smoke, and there is a saving in coal consumption. The thickness of the fire should not be less than 5 to 6 inches, and shallow places must never be allowed to form. If they do an excess of air will pass through into the combustion chamber, and this will reduce the temperature of the hot gases, tend to retard perfect combustion, and raise the fuel consumption per ton of tar distilled. In theory, 12 lbs. of air are required for each 1 lb. of coal burned, but in practice it is necessary to supply 18 lbs. to 20 lbs. for this amount of coal. To obtain the proper quantity of air, careful attention must be paid to the manipulation of the flue dampers and the air grids on the fire-doors, as well as to the thickness of the fire and the regular cleaning of the firebars.

In the case of gas firing one of the first things to be borne in mind is the risk of explosion on lighting up if a very simple precaution is not taken, namely, that of placing a few shovelfuls of burning coal or some lighted cotton waste on to the floor of the furnace before turning on the gas supply. Often a small fire is lighted on the firebars of the still furnace, using slack, and when well alight the gas is turned on. Occasionally small quantities of slack are spread over this fire, so that the firebars are kept covered to a depth of about 2 inches.

Some prefer not to use a small coal fire, as just described, and yet retain the type of furnace employed for coal firing in case the gas fails. What is done in cases like these is to cover the firebars with firebricks, or to remove the bars and bearers and replace them with stopping. Of the two plans the latter is the better as it gives more furnace room and allows for a more satisfactory combustion. Whichever method is adopted the gas must be admitted gradually until the still fireman is satisfied that all the gas coming forward will be ignited.

As the gas-burners are supplied with air ports it is a much easier matter to regulate the air supply in order to maintain proper combustion than it is with a coal-fed fire. The proportion of air to gas is different to that necessary for the proper combustion of coal. Theoretically, for complete combustion, it is about an equal volume, and in practice very little more than this is required. The best results are obtained with gas burners when the gas is supplied to them under a constant pressure, but to do this it is necessary to put in a gasholder.

CHAPTER VIII

PLANT USED IN THE DISTILLATION OF TAR (*continued*)

A PREHEATER (see Fig. 46) is very similar in shape to a tar still, the only difference being that the bottom is flat. It is constructed of wrought-iron or mild steel plates, and of a size to hold a little more than the charge for the still to which it is attached. As wear and tear are not very great, plates of moderate thickness are used in its construction; mild steel plates of $\frac{1}{4}$ inch or $\frac{5}{16}$-inch are quite thick enough. The mountings consist of: (*a*) A cast-iron charge pipe block or stool with a 6-inch or 8-inch hole, to which the charge pipe is connected; (*b*) a small cast-iron swan neck fitted on to a cast-iron stool, for connecting to the vapour pipe, which in its turn is fixed to a common main leading to a condensing worm. The swan neck may be 4 inches bore at the inlet, tapering to 2 inches at the outlet. In the author's opinion 2-inch or $2\frac{1}{2}$-inch wrought-iron steam-pipe, extra thick quality, suitably bent and connected to a flange, serves this purpose quite as well. (*c*) A $1\frac{1}{2}$-inch cast-iron gland cock fitted near the top of the preheater, through which a dipping rod may be inserted in order that the workman can find out when the vessel is charged correctly; if desired, instead of a dipping tap a flange can be riveted on and fitted with a $1\frac{1}{4}$-inch plug, the plug being removed each time a dipping operation is to be carried out. (*d*) A wrought-iron screwed flange of 2-inch bore, to which is fitted a 2-inch wrought-iron overflow pipe. This pipe is connected to a common main leading to a special tar tank. The overflow outlet is placed in such a position that at the finish of a distilling operation a correct still charge of hot tar remains in the preheater. (*e*) A wrought-iron pipe of 3-inch bore, which is known as the discharge pipe, to which is connected a 3-inch cast-iron gland cock. This pipe is placed on the side of the preheater at the bottom. (*f*) A manhole of 18 inches by 12 inches with draw-up lid. (*g*) Two extra deep, screwed, wrought-iron flanges of 3-inch bore, one placed so that its centre is about 3 feet 6 inches from the bottom and on the same side as the discharge-pipe stool, and the other on the opposite side as near the bottom as possible. These are for the inlet and outlet of a condenser coil, which is fixed inside the preheater. (*h*) A safety-valve or other suitable contrivance.

The condenser coil is made of 3-inch wrought-iron steam-pipe, but it should be of extra thick quality, viz. $\frac{5}{16}$-inch, in order to reduce the repair bill. The coil suffers severely from internal corrosion, especially the top lap; and in the author's experience wrought-iron steam tube of ordinary thickness ($\frac{3}{16}$-inch) has corroded through on the top lap in less than six months, against eighteen months if $\frac{5}{16}$-inch tube is used. The length of the coil may be approximately 160 feet, arranged in, say, six laps. Investigations made by the author and others indicate that the corrosion of preheater coils is due chiefly to dissociated ammonium chloride and ammonium sulphide, the temperature at the top lap being particularly favourable to chemical action.

Some workers recommend the use of cast-iron coils in order to minimise the trouble caused by corrosion, but against the virtue possessed by cast iron of not corroding so rapidly as wrought iron, must be set the clumsiness of a cast-iron coil, owing to its heavier weight, the many joints which are unsatisfactory in a condenser coil, and the lower heat transmission of cast iron compared with wrought iron. Fig. 47 shows one method of introducing the condenser coil into the preheater. The preheater is erected in an elevated position, so that the condensing coil may

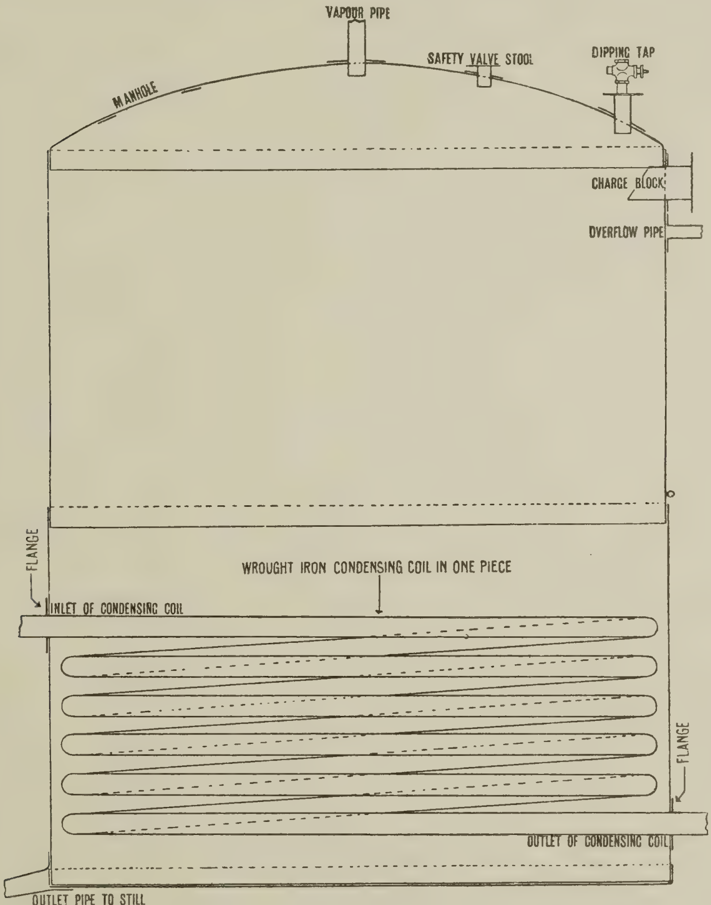

Fig. 46.—Diagrammatic Representation of Preheater.

be attached to the swan neck of the still, and the hot tar be discharged into the still by force of gravity. To secure efficiency it must be properly lagged with insulating material.

Several advantages are obtained by the employment of preheaters, the chief of these being: (*a*) There is a saving of fuel owing to the fact that hot tar is charged into the still, the tar absorbing part of the heat from the distillates passing through the preheater coil which otherwise would be lost; (*b*) the time of the distilling operation is reduced, as: (1) some of the entangled ammonia water is driven off; (2) a portion of the crude naphtha is distilled off; and (3) less time is taken to bring the still "round" (*i.e.* commence the distillation), owing to the tar being hot when charged into the still; (*c*) more tar can be worked in a given period, because it is not necessary for the tar still to cool down to any great extent before charging again, as would be the case if cold tar had to be dealt with.

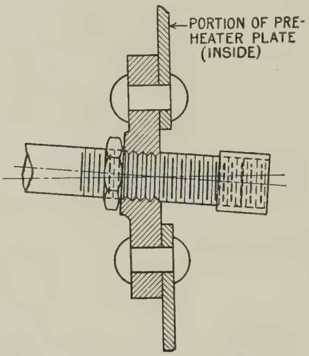

Fig. 47.—Method of introducing Condenser Coil into Preheater.

Connected to the outlet of the preheater coil, or, if a preheater is not used, direct to the swan neck, is the inlet end of the condensing coil proper. This piece of apparatus consists of laps of pipe, each lap being circular, square, or rectangular in plan, the circular type being the most general. A coil can be made of cast iron or wrought iron; the latter metal is preferable, as the thickness of a cast-iron coil and its lower power of heat transmission hinders somewhat the cooling or warming of the distillates, as the case may require. Another disadvantage in connection with cast-iron coils is the presence of a large number of flange joints, which introduces frequent trouble in the nature of leaking. Wrought-iron coils are manufactured of considerable length in one piece, and a coil of this kind will do away with the chances of the distillates leaking out, or the water surrounding the coil leaking in, as is so liable to occur in the case of flange joints. The internal diameter of condenser coils may vary between 2 inches and 4 inches, and the length between 130 feet and 300 feet, according to the size of the still. A distance of not less than $3\frac{1}{2}$ inches should be allowed between each lap, in order to provide a free circulation of cooling water, when this is passing through the condenser, and to facilitate the periodic cleaning of the outside of the coil by brushing down. A distance of 6 inches is allowed between the outside periphery of the coil and the side of the condenser tank. As an example, for a 20-ton still provided with a preheater about 130 feet of 3-inch wrought-iron pipe is sufficient. In order that the coil may be cleaned, it is advisable to arrange for a $\frac{3}{4}$ inch steam inlet, so that steam can be blown in after each operation. This provision will also assist in loosening a stoppage, should this occur. The steam inlet may be placed at the top of the coil before it enters the condenser tank.

The condenser coil is corroded from the top downwards, but not to such a great extent as the coil in the preheater. The corrosion also takes place from the outside as well as the inside, especially at the top lap at the "wind and water" line. On an average the top lap, if made of wrought-iron tube of $\frac{3}{16}$-inch in thickness, will last three years. It is possible to cut out the top lap when it is corroded through and join on a new lap; but if this is done, care must be taken to make a thoroughly good joint. The writer can recommend wrought-iron tube of $\frac{5}{16}$-inch thickness for the construction of a condenser coil.

The amount of cooling surface of condenser coils allowed at different works varies considerably. For instance, taking a 12-ton still, in one case 200 square feet in a water condenser, with 237 square feet in a preheater is allowed; while in another case 90 square feet in a water condenser, with 110 square feet in a preheater is made to serve the purpose; and in another case 146 square feet with no preheater is all that is considered necessary. This last figure is not to be recommended if a high degree of efficiency is required.

To calculate accurately the size of a condenser coil is not a simple matter as many factors are involved, some of which being of uncertain magnitude, and many physical constants which are required have not yet been determined. The subject of design of condensers will receive further attention in the chapter dealing with plant for the recovery of benzoles and naphthas; but the following figures, *which are approximate*, will no doubt be useful to the student.

Let it be assumed that it is required to find the length of a 3-inch condenser coil to be attached to a tar still of fifteen tons working capacity. Fifteen tons of tar on distillation will yield, say, 1,305 gallons of distillate, split up as follows :—

Crude naphtha	60 gallons or 552 lbs.
Ammoniacal liquor	83 gallons or 858 lbs.
Light oil	255 gallons or 2,573 lbs.
Middle oil, Creosote oil, and Anthracene oil .	907 gallons or 9,478 lbs.

The crude naphtha, ammoniacal liquor, and a portion of the light oil are reduced to a temperature approximating 60° F., but the other portion of the light oil and the middle, creosote, and anthracene oils leave the condenser coil at a much higher temperature than this, a fact which must be taken into consideration as indicated below. The steam to be condensed during the final stage in the distillation of the anthracene oil fraction has not been taken into account in this calculation; it is an unknown quantity as regards its amount.

CRUDE NAPHTHA.—552 lbs. to be cooled from, say, 370° F. to 60° F.

$$370-60=310^\circ$$

$$310 \times 552 \times \underset{\substack{\text{average}\\ \text{specific}\\ \text{heat}}}{0{\cdot}5} = 85{,}560 \text{ B.Th.U.}$$

+latent heat of vaporisation from boiling-point,
say, 153 $552 \times 153 = 84{,}456$ B.Th.U.

Ammoniacal Liquor.—858 lbs. to be cooled from, say, 212° F. to 60° F.

$212-60=152$

$152\times 858=130{,}416$ B.Th.U.

+latent heat of vaporisation from boiling-point

$=966$ $858\times 966=778{,}828$ B.Th.U.

Light Oil.—1,211 lbs. to be cooled from, say, 428° F. to 60° F.

$428-60=368°$

$368\times 1{,}211\times 0{\cdot}5=222{,}824$ B.Th.U.

+latent heat of vaporisation from boiling-point,

say, 153 $1{,}211\times 153=185{,}283$ B.Th.U.

1,362 lbs. to be cooled from, say, 464° F. to 100° F.

$1{,}362\times 0{\cdot}5\times 364=247{,}884$ B.Th.U.

+latent heat of vaporisation from boiling-point,

say, 153 $1{,}362\times 153=208{,}386$ B.Th.U.

Middle Oil, Creosote, and Anthracene Oil.—9,478 lbs. to be cooled from, say, 560° F. to 180° F.

$=9{,}478\times 0{\cdot}5\times 380=1{,}800{,}820$ B.Th.U.

+latent heat of vaporisation from boiling-point,

say, 162 $9{,}478\times 162=1{,}535{,}436$ B.Th.U.

Total B.Th.U. 5,279,893

The sum of the distillates equals 1305 gallons and the time taken for this quantity to distil over is, say, 18 hours.

$$\frac{1305}{18}=72{\cdot}5 \text{ gallons per hour (average)}$$

1,305 gallons = 5,279,893 B.Th.U.
72·5 ,, = 293,327 B.Th.U.

allowing 1,000 B.Th.U. per square foot of cooling surface per hour

$$\text{then}\ \frac{293{,}327}{1{,}000}=294 \text{ square feet of cooling surface}$$

$$\text{then}\ \frac{294}{0{\cdot}7854}=374 \text{ feet of 3-inch tubing.}$$

A portion of this tubing, say, 200 feet, can be fitted in a preheater, the balance of 174 feet being placed in a water tank and so constituting a water-cooled condenser. A more efficient method is to reduce the diameter of the pipe from 3 inches to 2 inches. This will mean 264 feet of 2-inch tubing instead of 174 feet of 3-inch. It is a good plan to place this in the form of D coils in a cylindrical water tank.

The condenser tank will vary in shape and size according to the type and dimensions of the coil it is intended to put into it, or whether the tank is to contain more than one coil. Generally the shape is cylindrical and of a size to contain one coil. Wrought-iron plate or mild steel of $\frac{1}{4}$-inch or $\frac{3}{8}$-inch thickness or cast-iron sections may be used to build the tank. In arranging for the size, due allowance should be made for water space between the outer edge of the coil and the tank side; 6 inches is a good margin. The bottom lap of the coil should not rest on the tank, but should have a clearance of between 4 inches and 6 inches. A 1½-inch drain cock should be placed in the centre of the bottom of the tank, by which to run off the water in case the tank or coil requires repairing, or when the tank and outside of the coil require cleaning. A hole must be cut in the tank bottom, through which to put the coil end. A good cold-water supply should be run to the tank, and the inlet pipe must extend to within 3 inches from the bottom of the tank, and it is a wise procedure to distribute the cold water as it flows into the tank. This can be done by fitting to the end of the inlet pipe a criss-cross of four pieces; if the inlet is a 1½-inch pipe then the four pieces should be of ¾-inch internal diameter. About 2 inches from the top of the tank the water overflow pipe is inserted; it should be so arranged that practically all of the top lap of the condensing coil is covered with water. The water inlet and overflow pipes may be of 1½-inch or 2-inch internal bore. It is necessary to place a perforated steam coil of one turn on the bottom of the tank, and a 1-inch steam-pipe is large enough. This is used to assist in raising

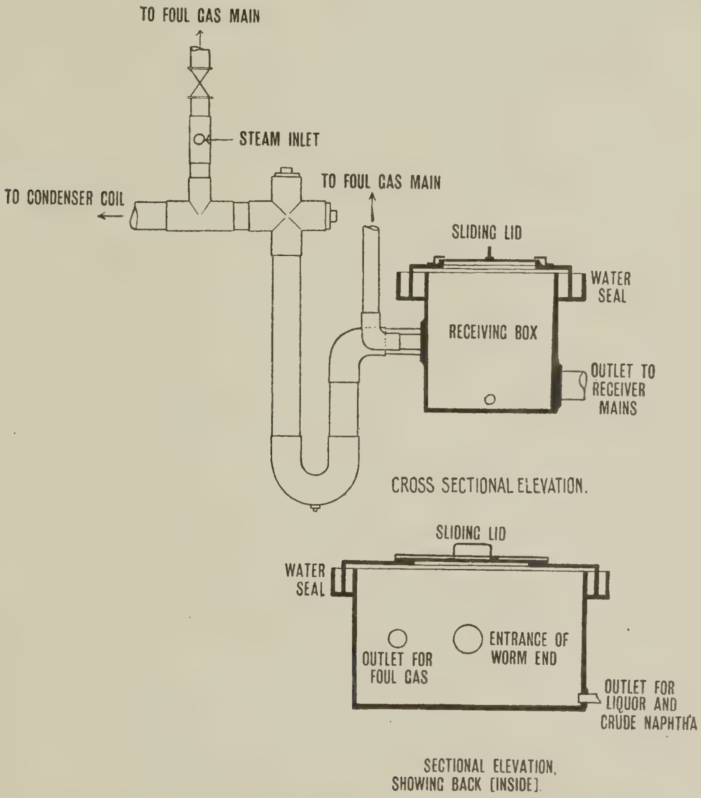

FIG. 48.—RECEIVING BOX AND CONNECTIONS.

the temperature of the condensing water at one period of the distilling operation, and also to aid in the removal of an obstruction of, say, creosote salts in the coil, should this occur.

The worm or coil end, after it leaves the condenser tank, is shaped in the form of a U in order to form a seal. One leg of the seal is connected to a small cast-iron tank known as a receiving or collecting box (see Fig. 48). This box should be covered with a cast-iron lid and water-sealed. In the lid a perfectly fitting sliding door is fitted (see Fig. 48), in order that the workman may inspect the distillates as they flow from the worm end, and also collect samples of them for testing purposes. The bearing parts of the slide and its frame should be kept thoroughly greased. Two outlets are made in the sides of the box, through which the distillates are run, and one outlet is provided for making a connection with the foul gas main. One of the distillate outlets is connected up to a piece of apparatus known as a dividing box, in which ammonia water is separated from crude naphtha, and the other to a pipe which is coupled up to the several receiver mains. Collecting boxes vary a little in size and shape, but for most purposes 2 feet 6 inches by 1 foot 6 inches by 1 foot 6 inches deep is quite large enough.

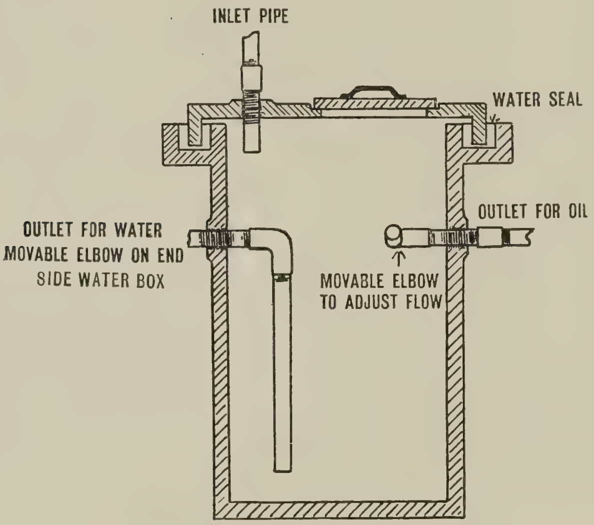

FIG. 49.—DIVIDING BOX.

The dividing box is made of cast iron, is cylindrical in shape, about 1 foot 9 inches in depth and 1 foot 3 inches in diameter. It is provided with a water-sealed cast-iron lid, in which is made a 6-inch inspection hole, covered with a lid, the bearing parts of which must be kept greased. There are two outlets, one which leads to a small piece of apparatus known as a water box, really a water-sealed inspection chamber, on the ammonia water main, and the other is connected up to the main which leads to the crude naphtha receiver. Each outlet is made of a sufficient size to insert a 1-inch wrought-iron pipe at about 4 inches from the top of the box. The centres of the two holes are on the same level, and the outlet pipe which conducts the crude naphtha away just enters the cylinder, and on to it is fitted a movable elbow to regulate the flow somewhat, while that which deals with the ammonia water bends down inside the box and reaches to within 1½ inches of the bottom (see Fig. 49). The inlet pipe from the collecting box is of 1-inch wrought-iron pipe, and is inserted in the cover of the dividing box. A wrought-iron connector should be placed in this pipe in order to facilitate removal if it becomes necessary to uncover the box.

The water box or inspection chamber (see Fig. 50) is a small cast-iron vessel about 8 inches by 8 inches by 8 inches deep, internal dimensions. It is provided with a cast-iron lid, water-sealed, and one 1-inch inlet hole at the side near the top, and another 1-inch outlet hole at the bottom on the opposite side. Through the inlet hole is inserted the ammonia water pipe coming from the dividing box, and on to the end of the pipe is fitted a movable elbow to enable the workman to regulate the flow of the liquor. To the outlet is fitted a 1-inch wrought-iron pipe, which leads to the common liquor main running to the ammonia water receiver.

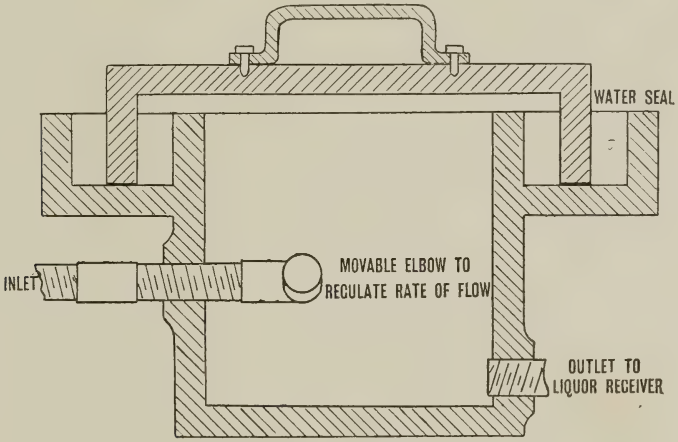
WATER SEAL
MOVABLE ELBOW TO REGULATE RATE OF FLOW
INLET
OUTLET TO LIQUOR RECEIVER

Fig. 50.—Water Box.

In some tar distilleries instead of connecting the worm end to the pieces of apparatus just described, a U seal is made in the condenser tube about 18 inches from the point at which it leaves the condenser tank, and following this the end of the tube dips into a sight or inspection funnel made of wrought or cast iron, and covered with a movable lid. This arrangement is to enable samples to be taken or an inspection made with ease. The funnel is connected to a pipe, which in its turn is joined to a small distributing tank of mild steel. At the bottom of this vessel are several outlets provided with cocks through which the different distillates are released. These outlets are connected to mains which lead to the receivers. In an arrangement of this description the crude naphtha and ammoniacal liquor run into the same receiver and are separated after a period of settling.

To remove foul gases, a connection is made with the condenser tube just after it leaves the condenser tank and before the U seal.

In order to comply with the Alkali Act, it is necessary to prevent the discharge into the atmosphere of all offensive or noxious gases, such as are given off from tar distillates, especially at the worm end, and to render these gases innocuous in some suitable manner. The plant used in tar works for this purpose varies somewhat according to the ideas of the management. In all cases it is necessary to provide foul-gas mains, to conduct away the gases and fumes from (*a*) the worm ends and collecting boxes; (*b*) the receivers; and (*c*) the pitch coolers. Lengths of 2½-inch or 3-inch wrought-iron pipe are fitted in close proximity to the various pieces of apparatus just mentioned, forming common mains, and the worm ends, collecting boxes, etc., are connected to these mains by means of T-pieces. One end of the common main is connected up to a steam-pipe, so that steam may be blown through frequently for cleansing purposes, and the other end to an exhaust pump or steam ejector, either of which draws away the foul gases, and delivers them to the boiler furnace to be burned, or to a special apparatus for treatment with a view to recovering sulphur, etc. In all cases in which it is intended to burn the gases it is advisable to draw them through a water seal of a design somewhat similar to a wash-bottle (see Fig. 51). This precaution will minimise the risk of a "flash back" taking place throughout the whole system. It must be remembered, however, that if the ejector is not carefully attended to, the risk of a "flash back" taking place and producing an explosion in the seal pot is great. The seal pot should be kept filled with water to three-parts of its depth, and in the cover a hinged lid is fitted, and always kept unfastened; the bearing parts being well greased with heavy lubricating oil to make a more or less tight joint. The author's experience of this method of dealing with foul gases has been a satisfactory one. A good plan, in order to see whether the exhausting apparatus is working efficiently, is to fit one or two manometers into the main in suitable positions.

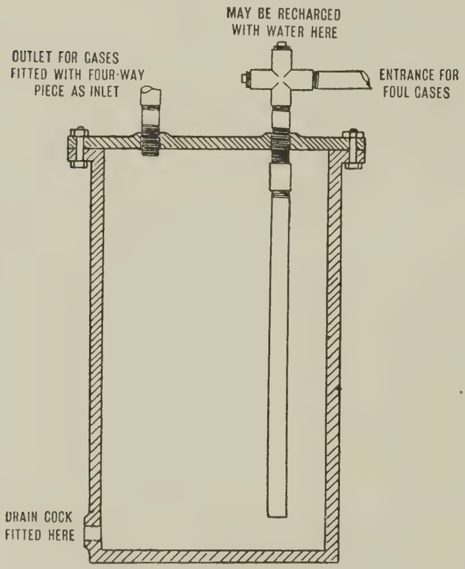
MAY BE RECHARGED WITH WATER HERE
OUTLET FOR GASES FITTED WITH FOUR-WAY PIECE AS INLET
ENTRANCE FOR FOUL GASES
DRAIN COCK FITTED HERE

Fig. 51.—Seal Pot for Foul Gas Main.

Owing to the corrosive action of the foul gases, the wear and tear on the cones of the ejector is very considerable. The author strongly recommends the use of malleable iron cones in the place of gun-metal, which is often used. The figures given in Table 56, the average of several experiments, will support this recommendation.

TABLE 56

	Gun-metal.	Malleable iron.
Diverging cones lasted . .	6 months	13 months
Converging cones lasted . .	8 ,,	24 ,,

Some distillers prefer to deal with the foul gases by passing them through an oxide purifier, more or less similar to a gasworks plant but on a smaller scale. The oxide is revivified as usual, and eventually sold for the manufacture of sulphuric acid.

A method of purifying foul gases by scrubbing with water and then passing through absorbing towers containing hydrate of iron in suspension in water was devised by J. Craven and W. H. Coleman, and published by them in the *Journal of the Society of Chemical Industry*, vol. 20. p. 200. This method is certainly a very safe one, and by it any ammonia, light hydrocarbons, and sulphur in the gases are recovered.

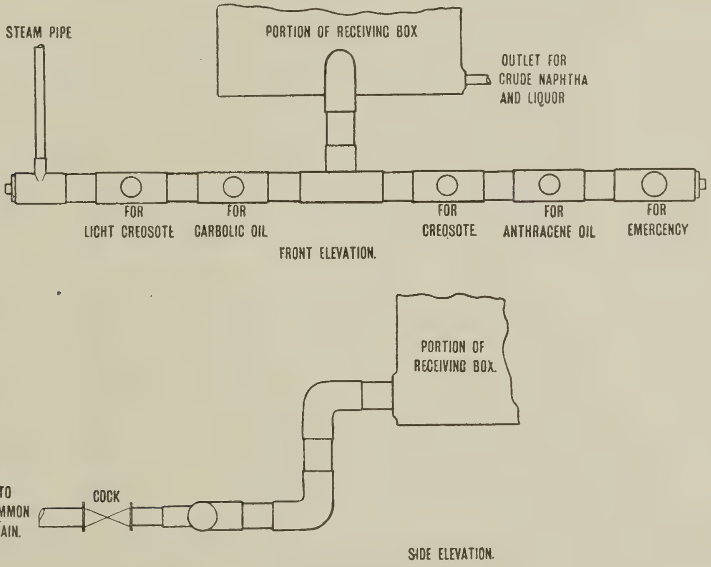

FIG. 52.—ONE METHOD OF CONNECTING COMMON MAINS TO RECEIVING BOX.

The various distillates from a battery of tar stills are led from the collecting or separating boxes to common mains, the latter being connected up to the receivers. Each of these common mains should be provided with a 1-inch steam inlet at one end for the purpose of introducing steam for cleaning after each operation, and to assist in removing obstructions should these occur. Endeavour should be made to keep the cocks which control the flow of the various distillates from the collecting box to the common mains as near one another as possible, and they should be suitably marked ; it saves time and prevents mistakes. A method of doing this is shown in Fig. 52.

The internal diameter of the common mains will vary according to the number of stills feeding them at one time; from 2 inches to 3 inches is generally found suitable. Connections between the collecting boxes and common mains may be of $1\frac{1}{2}$ inches to 2 inches internal diameter.

Good cocks should be put into all these mains, and also all the pumping mains about a tar distillery. Those made of cast-iron are the best to use, and the most satisfactory type is that known as the Butterfield cock. Generally cast-iron gland cocks are employed, but unless the glands and packing are carefully and periodically attended to, leakage of a more or less serious character will take place. A cock of the Butterfield type (see Fig. 35), if properly put in, requires very little attention, and it will not leak even in a main through which hot creosote oil and steam are continually passing. The author has in his experience known gland cocks to require attention every two or three days, and the packing seeing to about every month, whereas a Butterfield cock put in the same main required no attention or packing for a period of one year and nine months. No leaking took place from the latter cock, but from the former serious leaking often occurred.

It is, of course, necessary to provide a receiving tank for each fraction taken off the tar. The number will, therefore, vary according to the manner in which the tar is worked up, or the nature of the tar distilled. Generally there are seven receivers provided, one for overflow tar and one for each of the following distillates: ammoniacal liquor, crude naphtha, light oil, middle oil, or carbolic oil, creosote, and anthracene oil. Flat-ended boiler tanks (*i.e.* old steam boilers from which the tubes have been drawn and the ends blanked) make very suitable receivers. They must, of course, be in first-class condition, free from poor seams or thin plates. It is not possible to give any definite figure as regards size, as this must necessarily vary according to the quantity of tar worked per day and the amount of storage room. For a works distilling, say, 100 tons of tar per day, receivers of an average capacity of 8,000 gallons will be found quite suitable. Some works use specially made tanks of a size just sufficient to hold a little more than one of the various fractions worked off a single charge of tar. This, it is contended, enables the manager and workmen to check in a more efficient manner the yield of the several fractions from the tar.

All but the crude naphtha and ammonia receiver should be provided with a closed steam coil. One turn of 1-inch steam-pipe covering the whole bottom of the receiver will be found sufficient, provided an efficient steam trap is connected with the exhaust end. Each receiver must have a manhole, which, with all the other openings, should be properly covered, to prevent loss by evaporation in the case of the light distillates, and in all cases the escape of foul gases. It is desired by some to connect all the receivers to a foul gas main, but this is not absolutely necessary if all the openings are kept well covered. The contents of the receivers are removed to storage tanks, or washing tanks, by: (*a*) pumps, or (*b*) compressed air. In the latter case it is necessary to supply an air inlet, and also an exit pipe, which must reach to within about half an inch of the bottom of the lowest portion of the receiver. It is much better to put in a small dish plate at the bottom, as shown in Fig. 53. Arrangements must be made to seal the receiver completely; if this is not done removal by compressed air becomes an impossibility. For the compressed air pipe, 1-inch steam tube is quite suitable, and for the delivery or exit pipe, 2-inch steam tube is the best size to employ.

If it is desired to remove the receiver contents by the aid of a pump, then a 2-inch suction pipe should be put in. This can be arranged so that it will reach to the bottom, or be lifted to any point in the receiver. It is a general plan to connect the suction pipe of all the receivers to a common pumping main and pump, cleaning the two latter by blowing steam through after the pumping operation is finished. In all cases a special pump and main should be provided to deal with the crude naphtha, as it is unwise to contaminate this material with the heavier distillates. Although not absolutely necessary, it is a good plan to connect each receiver to a special emergency main and pump; it sometimes comes in handy when working difficulties arise.

It will not be out of place here to consider briefly the subject of steam valves, in particular those used round about the tar stills, condensers, collecting boxes, receivers, foul gas mains, etc. The valve in general use is made of gun-metal, and is of course quite suitable for all positions where sulphuretted hydrogen, ammonium sulphide, or ammonia vapours are not in evidence. If these vapours come in contact with the gun-metal shell of the valve, very rapid corrosion will take place, and a fracture eventually occurs. Cast-iron or cast-steel stop valves do not corrode anything like so rapidly, and are, therefore, much more suitable. It is advisable to lag the valves, and also all the steam-pipes, with a non-conducting composition.

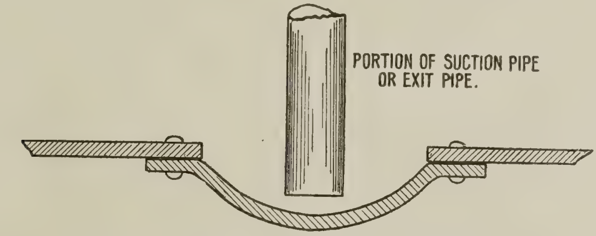

Fig. 53.—Dish Plate at Bottom of Receiver.

Owing to the high temperature at which it is necessary to run the pitch from the still, it is absolutely essential to keep it out of contact with the atmosphere and to cool it in some manner or other before running it on to the pitch bay. If this is not done, there is a great risk of spontaneous combustion of the hot vapours taking place, and a firing of the pitch; and even if the temperature of the pitch is too low for this to occur, acrid vapours are given off in great volumes, which will cause a nuisance in the neighbourhood of the distillery. In order to meet these requirements coolers made of wrought iron or mild steel, cylindrical or square in shape, are most frequently employed. The former shape is, of course, the most suitable, as it withstands much better the great strain brought about by running the very hot pitch into the cool receiver. A cooler is provided with a manhole of not less than 18 inches by 12 inches or 18 inches in diameter; a manlid stool, and cast-iron lid; an inlet pipe stool, to couple up to a 4-inch or 6-inch pipe, according to the diameter of the still tail pipe; an outlet valve of the "treacle" or gate type of about 6 inches, or of the lever plug type and not less than 4 inches; and a 2-inch outlet for connecting up to a foul gas main. The manlid is left loose in order to act as a kind of safety-valve, and it may be sealed by embedding into a lime-putty, or covering the bearing surfaces with a layer of thick grease. Old cylindrical steam boilers, from which the tubes have been drawn, and the ends blanked, answer admirably as pitch coolers, provided the plates are thick enough, and the riveted seams are in good condition. The plates of the cylinder should be of not less than $\frac{3}{8}$-inch and the ends $\frac{1}{2}$-inch in thickness, or better still a thickness of $\frac{1}{2}$-inch throughout. Each cooler should be raised a little above the ground level, say, 1 foot 6 inches to 2 feet, to allow inspection for leakage to be made, and also to enable the air to circulate all round it. It may be supported on brick or concrete cradles. A fall towards the outlet of about $\frac{1}{2}$-inch to the foot should be allowed.

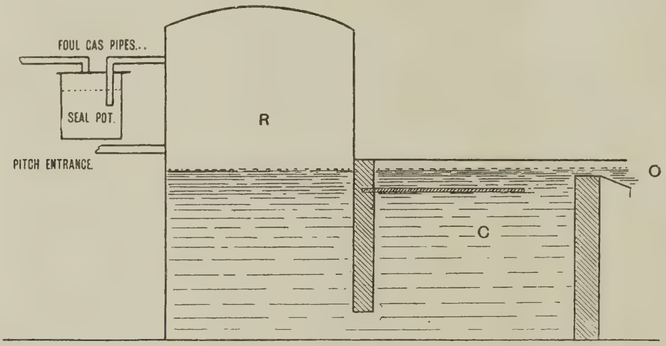

Fig. 54.—French Weir for Pitch-cooling.

Pitch coolers are sometimes built in the form of brick chambers, but as it is not a general practice this form will not be considered.

In a works dealing with large quantities of pitch, a pitch cooler built on the plan known as the "French weir" will give excellent results. There are two chambers in this cooler (see Fig. 54), that marked R in the figure being the one into which the hot pitch is run from the still and in which part cooling takes place. In the other chamber, marked C, the cooling is completed. When a fresh charge of pitch is run into R it pushes the cooled pitch contained in C through the outlet O into the pitch bay.

In order to convey the pitch from the coolers to suitable positions in the pitch bay, where the final cooling and solidifying prior to "getting" or digging takes place, a gutter is often built under the outlets of the coolers. The gutter should be provided with several outlets closed with gate or sluice valves, in order to direct the pitch into one portion of the bay to cool and solidify, while "getting" is being carried on in another portion. As regards the arrangement of this gutter, this will, of course, have to be made to suit the position of the coolers, and varies in different works. Concrete may be used to construct the gutter, the surface being rendered with a mixture of cement and sand, but it is far better to line the gutter throughout with brindled tiles or smooth bricks set in cement, as by doing this the removal of cold pitch during cleaning is facilitated. A depth of 2 feet 6 inches to 3 feet is ample, and it should be level from one end to the other. The sides of the gutter may be 14 inches or 18 inches thick, not less than the former. It should be so arranged that the gate valves can be operated by the workman in safety from a position opposite to that which the pitch runs into the bay. A method designed by the author is shown diagrammatically in Fig. 55. The gate may be raised and lowered by means of a rack and pinion or worm and wheel gear. In some works gutters are not used, but one is cut in the cold pitch on the bay in any desired direction. This is not a good plan.

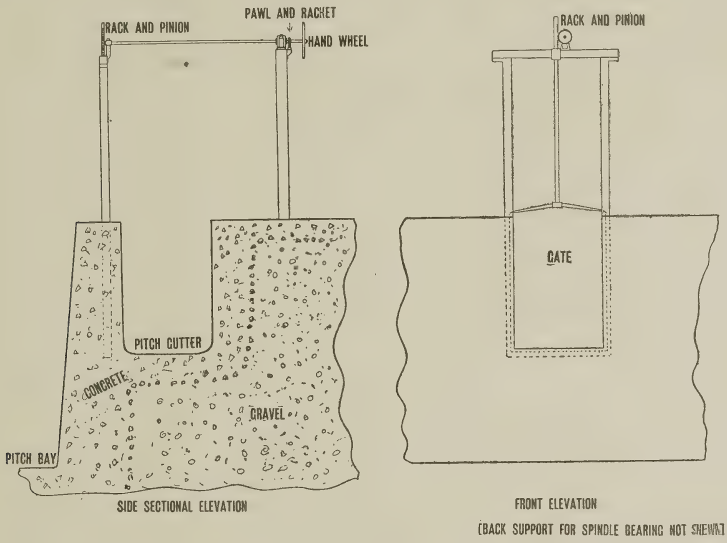

Fig. 55.—Pitch Gutter Outlet showing Gate Valve.

The pitch bay is situated in close proximity to the coolers at a lower level to them and the gutter. It must not be too deep, but of wide area, the dimensions varying according to local conditions and the amount of tar worked up. A depth of 2 feet 6 inches below the gutter outlets is a good average ; pitch of a greater thickness than 2 feet is more difficult and expensive to " get." The floor and sides of the bay are concrete or brick lined. As regards the floor, a brick lining placed on a concrete bed proves the most suitable, the bricks being smooth faced and of the best Staffordshire blue brick type. They should be set closely in good cement, and the whole floor made quite level. It is advisable to divide the bay into several sections, say, three or four, by building 14-inch walls across it. If it is wished to avoid the expense of doing this, temporary partitions can be put up with wooden planks and loose pitch, or by leaving a wall of hard pitch from a previous " getting," but these methods are of doubtful value, as the partitions sometimes give way at most inconvenient times. The object of dividing the bay into sections is to allow one batch of pitch to cool while another is in the process of "getting."

It is as well to endeavour to arrange for a private railway siding to run alongside the pitch bay, and it is of great advantage if that siding is at such a level that the top of the railway trucks are practically in line with the floor of the bay. This will enable the pitchmen to wheelbarrow the pitch direct into the trucks and save the cost of a crane, skips, and a crane driver.

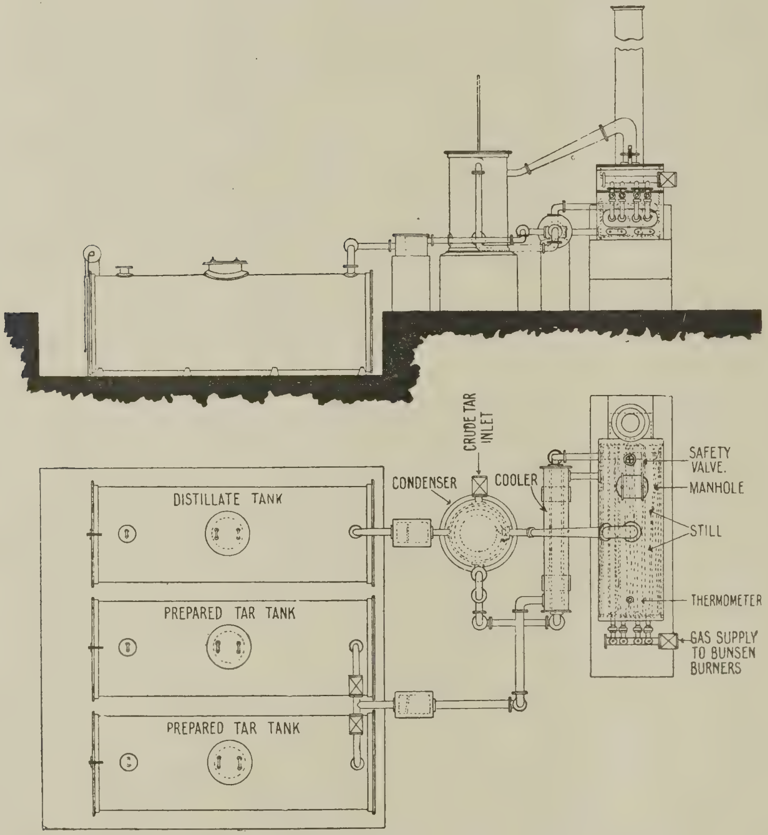

FIG. 56.—DIAGRAMMATIC ILLUSTRATION OF HIRD'S TAR-DEHYDRATING PLANT.

There are times when a tar still springs a leak, and it then becomes necessary to empty that still with all speed. In order to do this a permanent 3-inch wrought-iron main should be run along the back of the battery of stills, and a branch from this main fixed in a suitable position, so that after the connection between the tail or run-off pipe of the still and the cooler is taken apart, immediate connection with this branch can be made. One end of the main should be closed with a plug, and the other end connected to a special pump kept especially for emergencies of this nature.

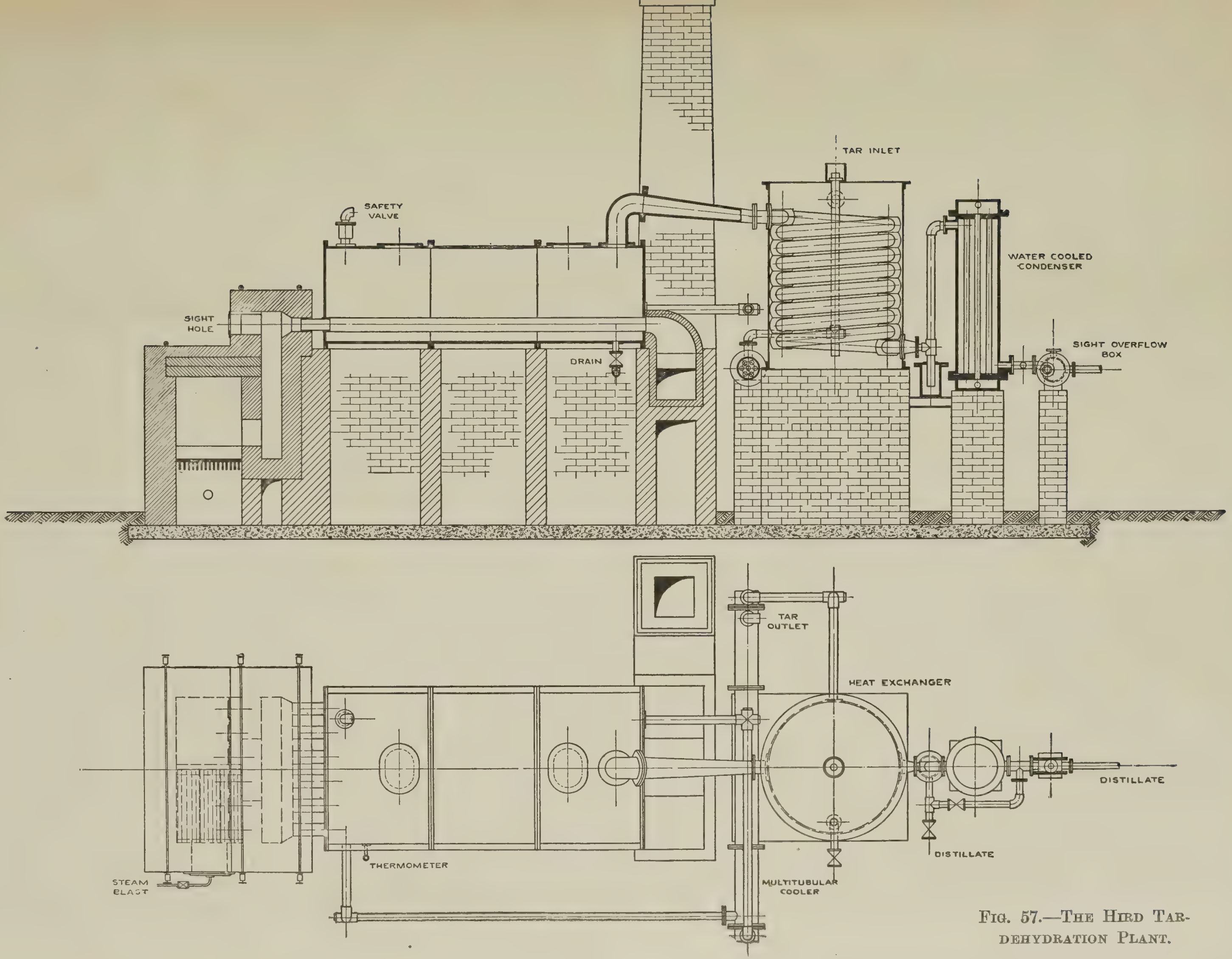

FIG. 57.—THE HIRD TAR-DEHYDRATION PLANT.

The same pump can be used, if desired, as an auxiliary to the creosote pumps, but should always be so connected that it can be put into use on the tar emergency main immediately it is required. If the tar well is below ground, a pump is not absolutely necessary, as the still being above ground level, the tar would run by force of gravity into the emergency main and thence to the well. However, speed is a matter of importance at times, and then a connection to a pump would prove of benefit, even when the tar well is below ground.

Plants for the dehydration of tar have of late come much to the fore, and a brief description of three of the chief types of this class, viz. Hird's, Wilton's, and Chambers and Hammond's, will, no doubt, prove useful to the reader.

The following is a brief description of Hird's dehydrating plant, capable of dealing with half a ton of tar per hour. This plant consists of the following pieces : one still, a cooler, one condenser coil and tank, one distillate tank, and two prepared tar tanks, with the necessary pipes and connections (see Figs. 56 and 57).

The still, which is constructed of cast iron, has fitted down the centre a longitudinal baffle, the function of which is to direct the tar first down the length of one side of the still and then up the other side. Four tubes, which are expanded into the end plates, run the whole length of the still, for the purpose of carrying the hot gases with which to heat the tar. A brickwork furnace is built up to the end of the still, so as to deliver directly into the heating tubes. Otherwise bunsen burners may be applied directly to the ends of the tubes. To the still is fitted a swan neck and safety-valve, and it is also provided with a manhole and manlid, and a thermometer for regulating the temperatures.

Between the condenser and the still is fitted a cooler, or rather a heat interchanger, which consists of a nest of steel tubes lying inside an outer C.I. casing. Tar from the condenser tank travels through the inner tubes on its way to the still, while the hot prepared tar flows through the outer tube or jacket on its way to the receiver.

The condenser tank is cylindrical, and is provided with an inlet and outlet for cold tar, which is used for cooling. In this tank is placed a cast-iron condenser coil, the top of which is connected to the vapour pipe leading from the still, while the bottom is joined to an inspection box, which in its turn is connected to the distillate receiver.

At this point a brief description of a very recent type of dehydrating plant designed by S. A. Wikner will not be out of place.

The "Wikner" Dehydrating Plant[1] employs steam-heating tubes at boiler pressure, laid horizontally in a steel or cast-iron chamber about two-thirds full of tar. The steam tubes all lie in the top two or three inches. Hence, quite a small proportion of tar is actually boiling, this explains how the frothing difficulty is got over.

The water and naphtha vapour which are released are condensed by passing down coils immersed in the cooler layers of tar below the heating tubes. These

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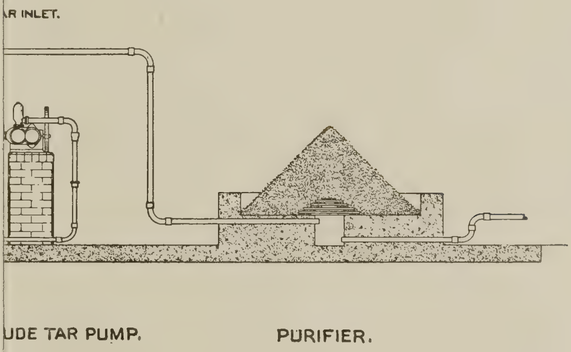
[1] See also "The Preparation of Road Tar in Gasworks," S. A. Wikner, *Gas World*, May 13th, 1922, pp. 403–406.



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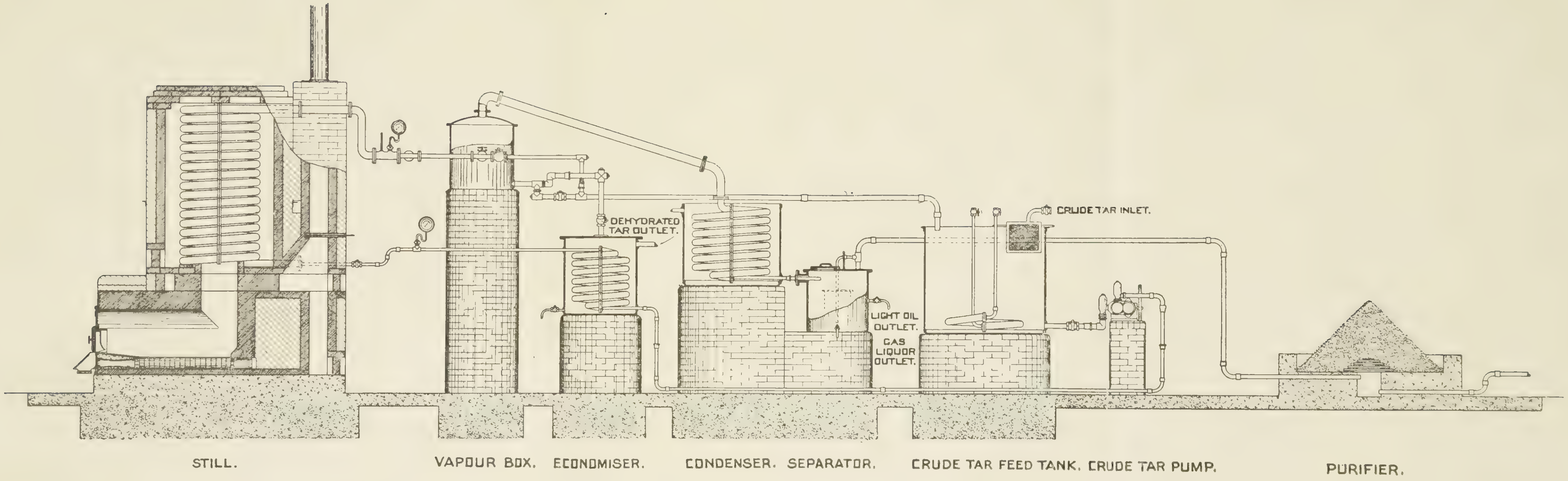

Fig. 58.—Wilton's Tar Dehydration Plant.

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vapours do not leave the still as such, as the condensing coils open directly into the space above the tar.

The whole principle depends on the fact that the fuel efficiency of a boiler is normally higher than that of tar dehydrating plant in general, partly on account of the scale of handling being larger, and also of the inherent possibilities of the boiler in this direction.

The fuel costs of dehydration, therefore, by this plant are very low and cannot be attained by direct-firing methods: the labour cost for firing and attention is also greatly reduced.

Another advantage is that the plant can be shut down and started up at short notice, as without any direct attention full steam can be left on without serious loss for any desirable time. There is obviously a reduced accident risk.

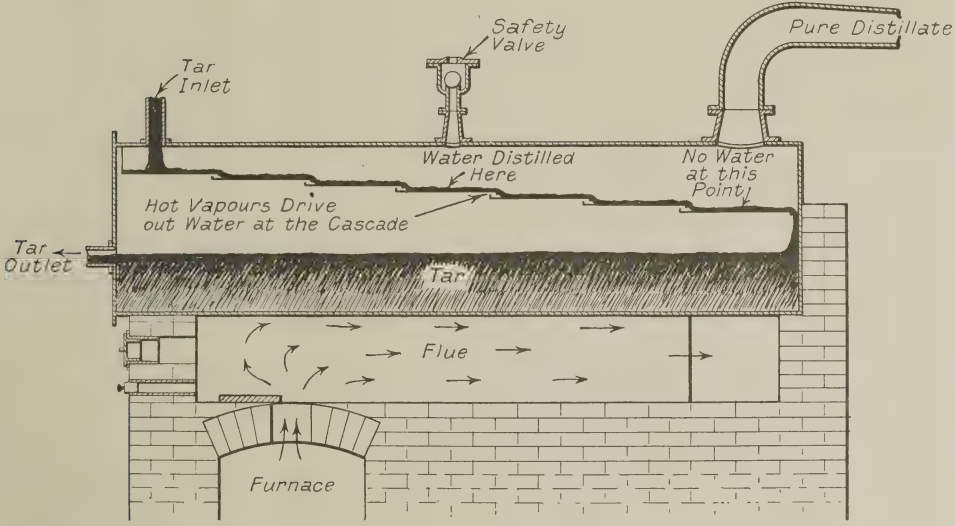

FIG. 59.—PATENT CASCADE TYPE OF STILL FOR CONTINUOUS TAR DEHYDRATION OR DISTILLATION PLANT. (CHAMBERS AND HAMMOND.)

The plant was designed originally to run in conjunction with the complete Hird Tar Distilling Plant, and it was found that the result of feeding the latter with hot dehydrated tar was nearly 100 per cent. increased daily capacity.

The Wilton Tar Dehydration Plant is continuous in its actions, separating out the light oils, water, and dehydrated tar in a continuous stream for immediate use or storage in separate vessels. This plant is simple in construction and economical in working, and owing to the small amount of tar passing through the plant at a time the fire risk can be considered as entirely absent. Dehydrated tars to answer to the specifications of the Roads Board can be prepared by this plant.

The general method of working of the Wilton plant is as follows: The crude tar is forced through the plant by a pump (see Fig. 58) first entering the coil of the economiser. This coil is surrounded by hot finished dehydrated tar, and much of its heat is given up to the crude tar as it passes through the coil on its way to the still. The still consists of a number of cast-iron coils superimposed one above the other and set in a furnace heated by a fire of coke or breeze. Tar enters the still at the bottom and passes upward gaining heat on its journey. On leaving the still its temperature is approximately 140° C. and it is at a pressure of between 30–40 lbs. per square inch. (These figures are varied somewhat according to the fractions required.) It should be noted that pitching is practically impossible owing to the speed of circulation of the tar in an upward direction in a confined space.

On leaving the still the tar enters a cylindrical vessel with a dome-shaped cover called the vapour box. Here, the pressure being released, the tar expands suddenly under atmospheric pressure, and water and oil are volatilised. The mixed vapours pass along a vapour pipe to a condenser, and the liquids leaving the condenser run into a separator which divides the light oil from the gas liquor.

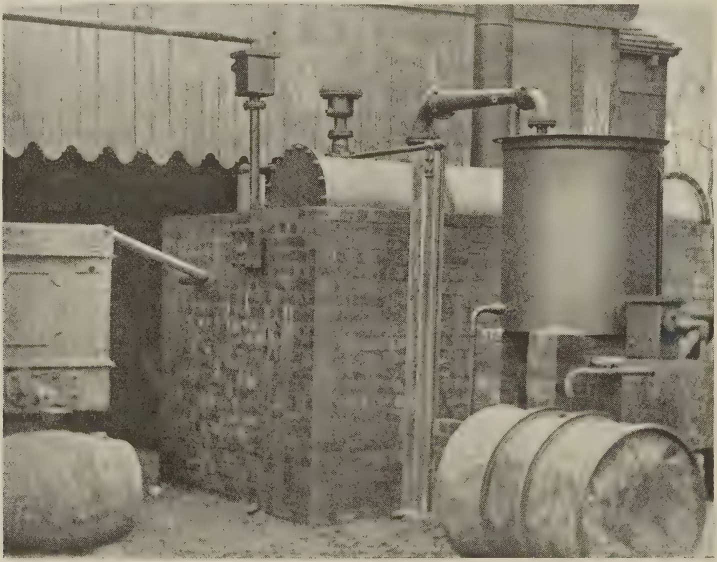

Fig. 60.—Patent Cascade Type Continuous Tar Dehydration Plant. (Chambers and Hammond.)

The dehydrated tar gravitates from the vapour box to the economiser and thence to storage tanks.

The Wilton plant can be built to deal with any output from 100 gallons an hour upwards, and the design modified to extract up to 50 per cent. water and light oils. It is possible to use standard units of this plant for the purposes of (1) Debenzolising wash oil ; (2) Topping creosote oil ; and (3) Topping crude light oil.

In the Chambers and Hammond's patent cascade type of tar dehydrating plant, there is a distinctive feature embodied in regard to the separation of water for the elimination of "foaming."

Those who are familiar with the working of continuous tar dehydration plants know that when the ingoing crude tar is used for condensing purposes there is a tendency for the water in the crude tar to accumulate, forming "pockets" of water which occasionally pass forward to the still. As the temperature of the tar in the still is seldom below 200° C. it follows that, when the water comes into contact with the hot tar, "foaming" will occur.

In the type of still (Fig. 59) under consideration, matters are so arranged that "foaming" is eliminated. In the first place, crude tar is not used for condensing the light oils, and accumulations of water are thereby avoided, and in the second place the water contained in the crude tar is removed before it enters the body of hot tar in the still. This object is attained by fixing in the vapour space of the still a cascade or staircase, down which the crude tar must flow, in a shallow layer, before it can enter the distilling tar.

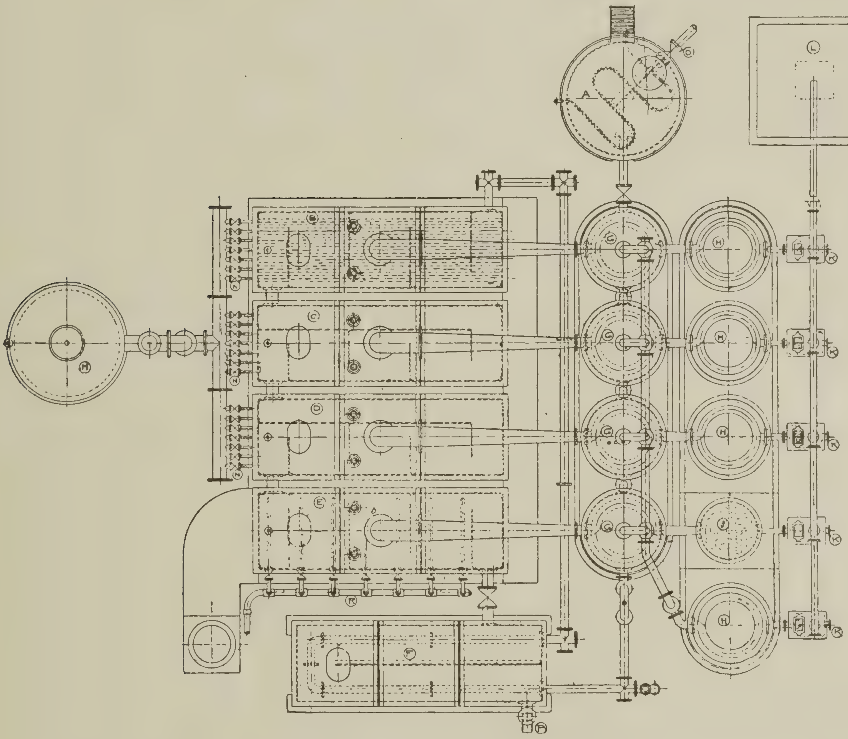

Fig. 61.—Plan of Hird's Continuous Tar Distillation Plant.

As a rule there are seven plates in the cascade, and a plant dealing with one ton per hour of tar will have seven plates, each 2 feet square and giving a total heating surface of 28 square feet. The depth of the tar on the cascade does not exceed half an inch, and by the time the feed tar enters the still proper the whole of the water has been distilled away.

This type of still may be heated either by gas or coke. In the latter case no special type of furnace is required. The still consists of a circular tube, with one end welded and the other end bolted on. There are no baffles or other obstructions in the bottom of the still, and accumulations of "free carbon" are thereby avoided.

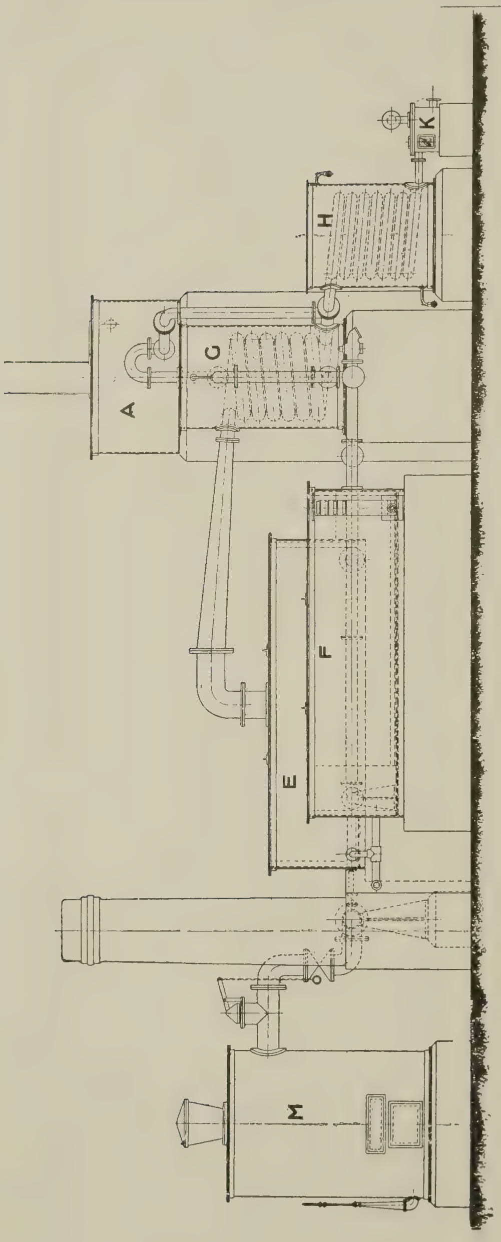

FIG. 62.—HIRD'S CONTINUOUS TAR DISTILLATION PLANT.
A, Tar Regulating Tank. E, No. 4 Still. F, Pitch Cooler. G, Combined Heater and Cooler. H, Coil Condenser. K, Sight Box. M, Gas Producer.

The still will work for several months without stopping for cleaning, and, when necessary, cleaning is easily carried out by first removing the end plate, when every part of the still is accessible.

Fig. 60 gives a general view of this type of dehydrating plant at work. The plant illustrated will distil five tons of tar in ten hours. This plant works in the daytime only, and is shut down at night-time.

The crude tar enters the plant at the sight feed box, and passes forward to the heat interchanger, which is arranged not only to take up heat from the hot dehydrated tar, but also from the waste furnace gases. Leaving the heat interchanger, the tar at a temperature of 100° C. enters the still and is delivered on to the top plate of the cascade, down which it flows until, leaving the last plate, it enters the still proper.

The tar flows forward from one end of the still to the other, and then out by a pipe to the heat interchanger. The distilled tar flows through the central pipe, and gives up a portion of its heat to the surrounding crude tar, which again is externally heated by the waste flue gases. The prepared tar is finally delivered into a receiving tank.

The vapours of light oil and water pass out by the still head to a water-cooled condenser and into

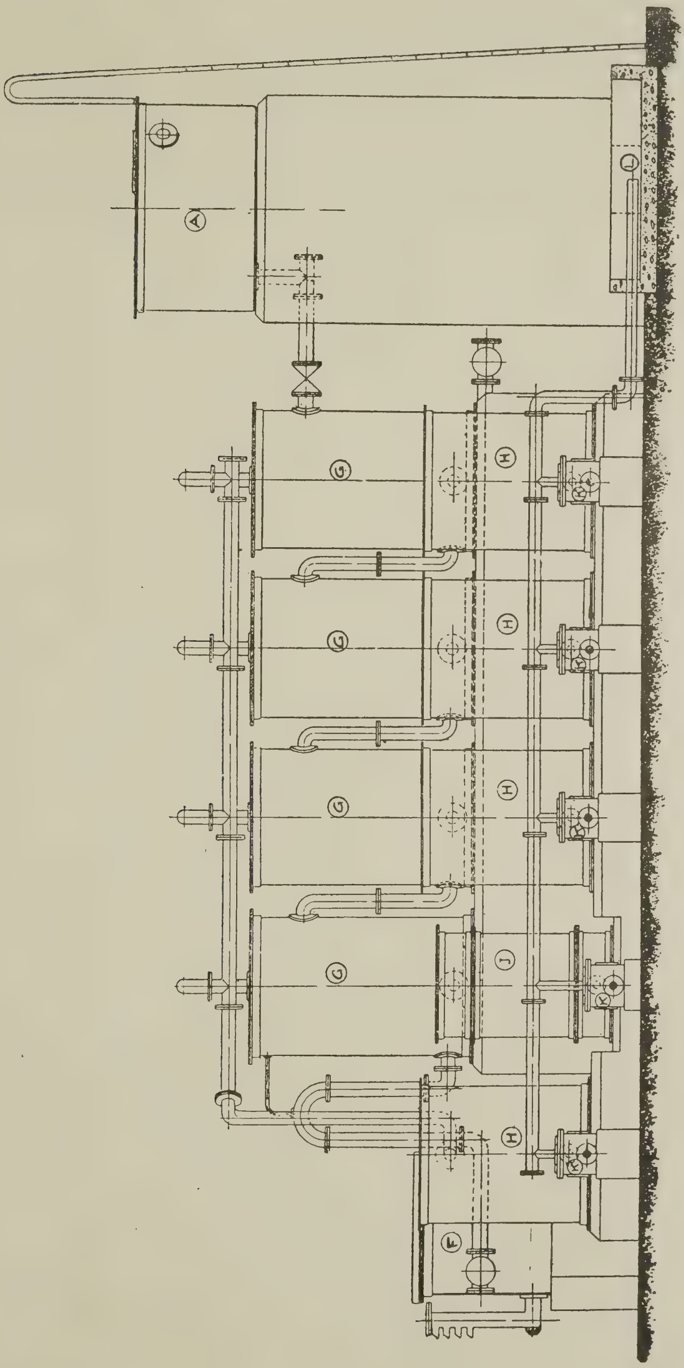

FIG. 63.—HIRD'S CONTINUOUS TAR DISTILLATION PLANT.

a separating box, which automatically separates the water from the light oils. In small plants the light oils may flow directly into steel drums or casks, but for larger plants storage tanks are necessary.

When dehydrating tar by the continuous process, the working temperatures necessary to provide tar in accordance with the Roads Board Specifications are :—

For tar spraying	(No. 1)	230° C.
For tar macadam	(No. 2)	260° C.
For pitch grouting	(No. 3)	288° C.

The continuous distillation of tar down to pitch is a process much older than that of continuous dehydration ; in fact, the latter is simply an offshoot of the former.

One of the earliest systems of continuous distillation which received any serious consideration is Lennard's (1888). The plant with which to carry out this system was designed on the cascade principle, was rather complicated, and was an expensive one to erect. More recently the Hird, Wilton, and the Chambers and Hammond systems have appeared, and the results obtained by them have proved very satisfactory.

Hird's patent systems (see Figs. 61, 62, 63, 64, 65, 66, 67, and 68) includes the following pieces of apparatus : A feed or regulating tank, a steam preheater, three or four stills, a pitch cooler, three or four combined heater-coolers, four or five water condensers of the coil type, sight boxes, an oxide purifier, and, if the plant be heated by gas or producer gas, gas burners are necessary, otherwise a pressure furnace for breeze firing is erected to deliver directly into the heating tubes. The feed or regulating tank is provided with a float valve in order to maintain a constant feed of tar to the stills.

Frequently all the stills are built of cast iron, as this material has the advantage of resisting almost completely the attack of ammonium chloride. The anthracene still, the last, is constructed of steel, as it is generally found in this type of plant that corrosion is quite negligible at the point of distillation process when the anthracene oil fraction is coming over. Each still is provided with a manhole, a swan neck and vapour pipe, a thermometer, and a safety-valve. Internally there are baffle plates fitted in such a manner as to cause the tar to flow in a circuitous manner from inlet to outlet. The arrangement of the baffle plates in Nos. 2 and 3 stills is rather different from that in Nos. 1 and 2 stills, as will be seen on reference to the diagram (Fig. 61).

The stills are provided with heating tubes of steel, expanded into the end plates, and on gas-fired plants a burner is supplied to every tube. The last or anthracene still has burners, but is also fitted with an arrangement of flues to permit of the use of waste heat from the rest of the plant. The tar enters at the first still and passes through the stills in succession, finally to a pitch cooler.

The pitch cooler is provided with a manhole, and fitted inside with a baffle plate so arranged that the pitch will flow up one side of the cooler and down the other before it leaves for the pitch bay. A steel coil is fitted inside the cooler and runs up one side and down the other. This coil carries the tar from the heater-coolers

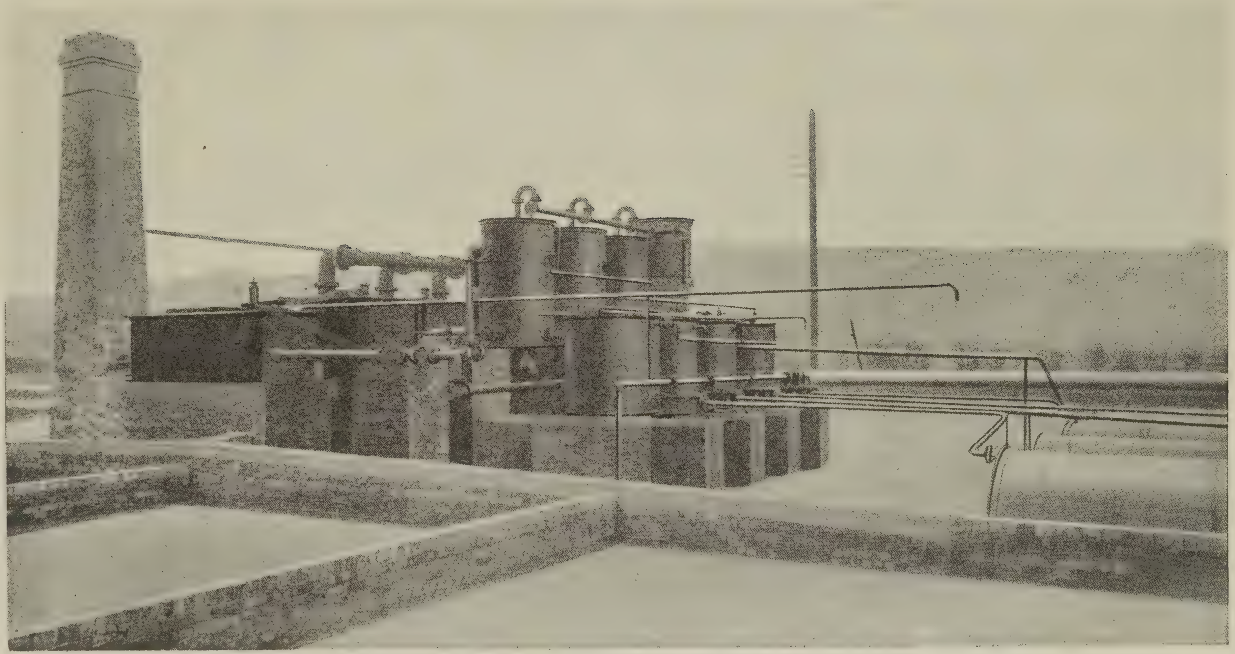

Fig. 64.—Hird's Continuous Tar Distillation Plant.

to the stills, reducing the temperature of the pitch in so doing. A weir valve is fitted to the outlet of the pitch cooler so that any seal of tar in this vessel can be obtained as desired, this being an advantage in working different classes of tar.

The heater-coolers consist of wrought-iron tanks, each provided with an inlet near the top and an outlet near the bottom, through which the crude tar is conducted on its way to the pitch cooler and the stills. Each heater-cooler is fitted inside with a cast-iron coil connected at the top to the vapour pipe and at the bottom to the top of the coil of the water condenser. As distillation takes place from the heater-coolers, each cover is fitted with an outlet connected to a common main which conducts vapours to a water condenser.

A feature of the more up-to-date plants is a steam preheater for the crude tar in the anthracene still, employing the steam, etc., which has not been condensed in the heater-cooler corresponding to the anthracene still.

The final condenser casings are constructed in wrought iron and fitted inside with cast-iron coils. The top of each coil is connected with the bottom of a heater-cooler coil, and the bottom of each coil to a sight box. Each condenser is fitted with inlet and outlet for water supply for the purpose of cooling the distillates.

Connected to the coils of the water condensers are sight boxes. These are provided inside with a seal to prevent foul gases from getting into the atmosphere. Each sight box is also provided with an outlet for the condensed distillates and another for the foul gas.

It takes about eight hours to get the plant into working order, after which only a very small amount of supervision is required. In this plant tar can be fractionated into ammoniacal liquor, crude naphtha, light oil, creosote oil, anthracene oil, and pitch, and the distillates leave the plant uniform in quality.

Considerable success has attended the use of the Hird distilling system in the redistillation of oils and heavy solvents, to free them from non-volatile residues and to regenerate them for use. The stills for these purposes are made generally of steel, and there are some minor variations of construction.

Wilton's Patent Semi-Continuous Tar Distillation Plant (Fig. 69) combines the pot still with the modern continuous system, incorporating the advantages of both. The chief of these are: (*a*) Large saving of fuel; (*b*) any number of cuts can be made; (*c*) variation of water content of tar does not reduce the through-put; (*d*) the tar is completely dehydrated before it enters the pot stills, consequently there is absence of priming or frothing; (*e*) the continuous dehydration of the tar ensures the maximum output through the pot stills; (*f*) the pitch can be tested from bulk and corrected, if necessary, before running off; (*g*) wear and tear on the pot stills is reduced considerably; (*h*) dehydrated tar can be made, if desired, by cutting out the pot still; (*i*) owing to freedom of frothing in the pot stills, a fewer number of these are necessary to distil the same quantity of tar.

The method of manipulating the plant consists in continuously dehydrating the tar in the Wilton Patent Dehydrator, which can be worked to any reasonable temperature at will, thus placing the dehydrating section under absolute control. The "boiling" dehydrated tar gravitates to one pot still, and when this is charged the

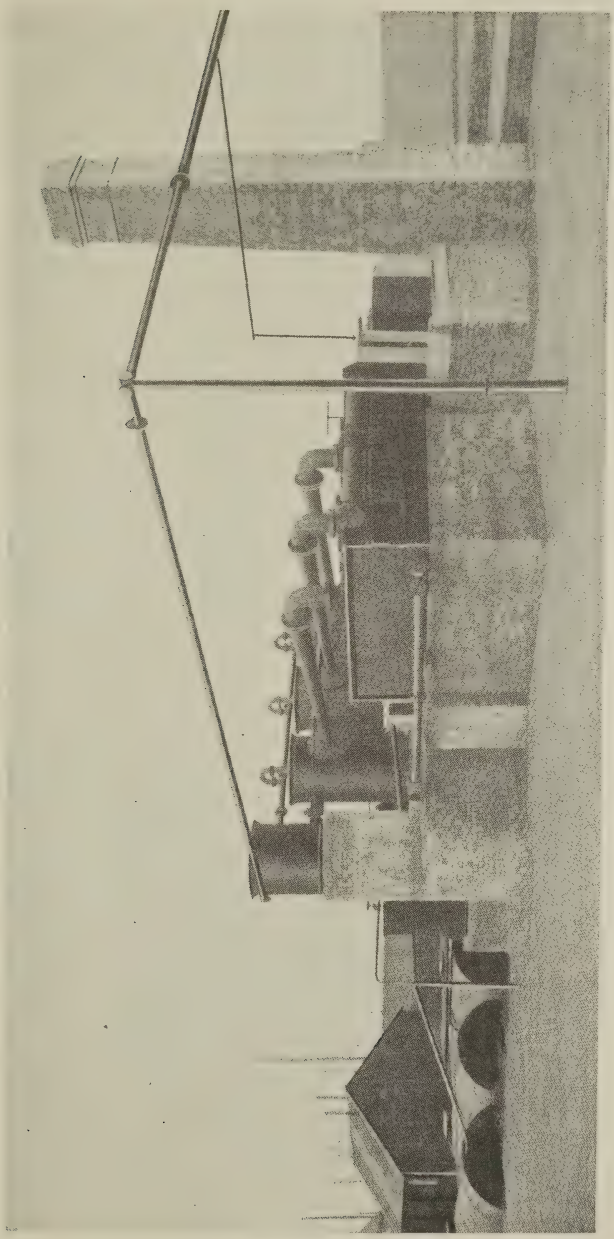

Fig. 65.—Hird's Continuous Tar Distillation Plant.

contents are worked off to pitch, whilst the dehydrated tar is diverted to another pot still, the charging of which is gauged so that the first still will be worked off by the time the second is charged.

In Fig. 70 is illustrated a later type of the Chambers and Hammond Continuous Tar Distillation Plant, which is of more simple design than its predecessors, and which possesses several distinctive features.

In the first place, there is a special method of dealing with the water contained in the tar; secondly, the stills are of a circular tube pattern, containing neither heating tubes nor baffle plates inside. With a view to working on a low fuel consumption arrangements are made for taking up as much waste heat from the system as is practicable. The plant consists of three circular stills, three rectangular condensers, and one heat interchanger, or pitch cooler. The plant may be heated either by gas or coke. It produces crude naphtha, light oils, creosote and anthracene oil. In the plant illustrated the light oils and crude naphtha are collected as one distillate.

The first still is fitted with a cascade, of the same type as that described previously in connection with the Chambers and Hammond Tar Dehydration Plant (see page 166). It has previously been pointed out that when the water has been removed from crude tar the subsequent distillation of the tar is not difficult to carry out, and this statement applies either to intermittent or continuous distillation.

Fig. 59 illustrates clearly the method adopted in this plant for disposing of the water problem. The details as to the working of the cascade have been explained in the description of the Chambers and Hammond Tar Dehydration Plant. The advantage of the cascade is very pronounced in the case of Mond or water-gas tar, and cases of "foaming" or sudden "priming," together with the accompanying lifting of the safety-valves, are not experienced. Distillation plants embodying this process are at work upon crude tar containing more than 30 per cent. of water.

The working of the plant is demonstrated by studying Fig. 71. Crude tar flows from the sight-feed inlet directly into the heat interchanger, which is designed to heat the ingoing tar, and cool the outgoing pitch. It consists of an outer tube 15 inches diameter, and a central inner tube 6 inches diameter, and is so fixed in the waste heat flue as to be entirely surrounded by the hot flue gases. The crude tar flows forward in the space between the two tubes, with the result that the crude tar absorbs heat, externally from the flue gases, and centrally from the outgoing pitch.

Leaving the heat interchanger the hot tar enters the first still, flows down the cascade and along the still. The depth of the tar is generally one-third the diameter of the still. The tar leaves the first still at its front end, flows through a pipe into the second still, being discharged at the back end of the still, where it again flows forward to the front end, passing through a pipe into the third still. The tar passes along the third still and is collected in a pipe, which conveys the resulting pitch back to the front end and out to the heat interchanger, after which it flows directly into the pitch beds.

Stills No. 1 and 2 are heated by direct heat, but the third still and the heat interchanger are heated by waste gases from the first two stills. In the case of

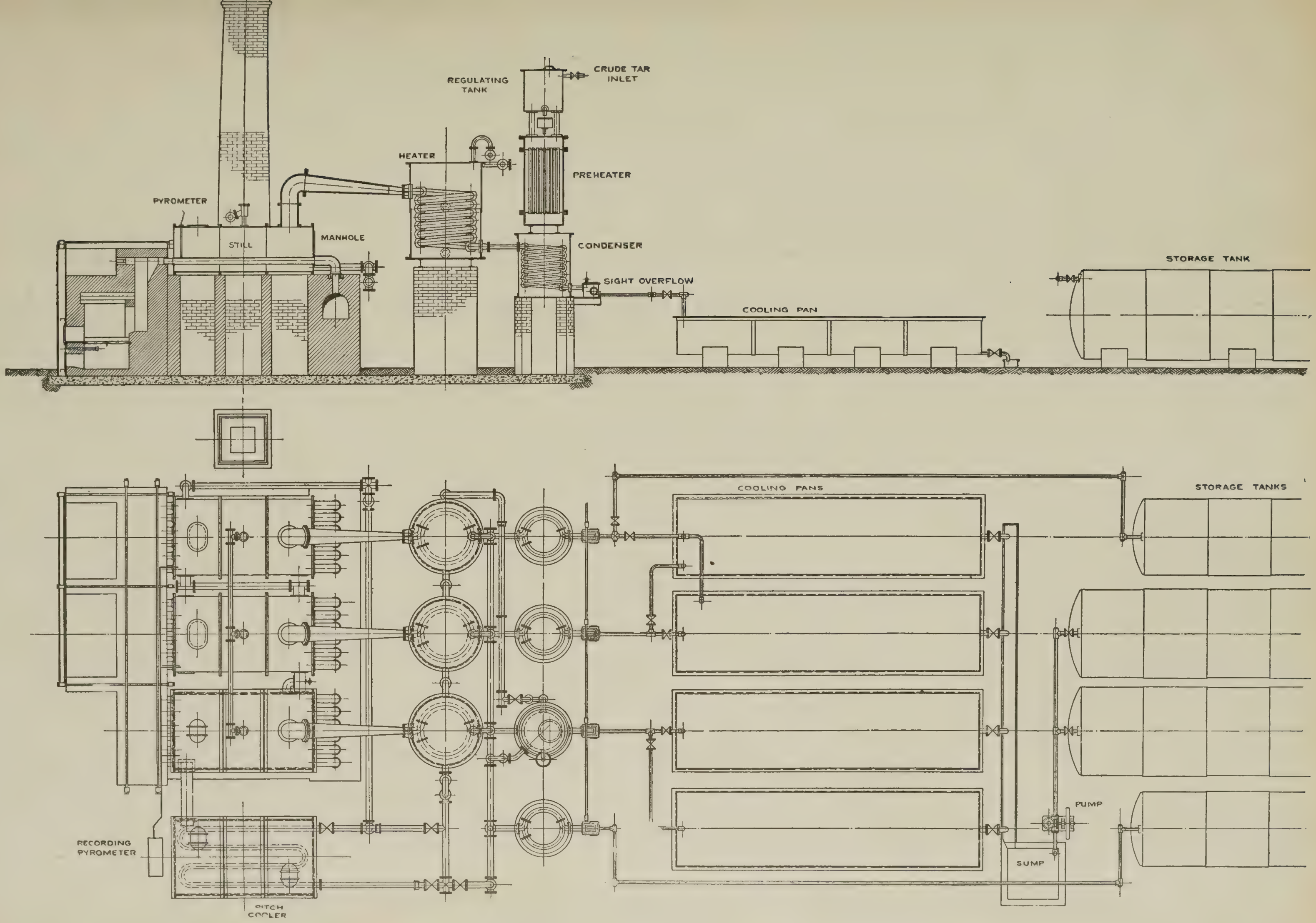

Fig. 66.—The Hird Tar Distillation Plant (Coke-fired Stills).

either gas or coke firing, there is a common firebox or combustion chamber for Nos. 1 and 2 stills.

The supply of heat can, however, be regulated to either still by movable dampers fixed over portholes in the curtain arch under the stills. The sliding dampers are operated from the front end of the still setting. There are only two portholes, one for each still. When gas firing, one larger, or several smaller gas burners can be fitted into the combustion chamber.

The fractions of distillates pass through tapering vapour pipes to rectangular condensers, fitted with "S" bend cast-iron pipes. Narrow condensers require less water than circular tanks for condensing purposes. After leaving the condensers the oils pass through cast-iron oil traps for separating foul gases, and the latter are dealt with in an oxide purifier. The working of the stills is controlled by thermometers at the front end, and a wide variety of fractions may be obtained by regulating the sliding dampers.

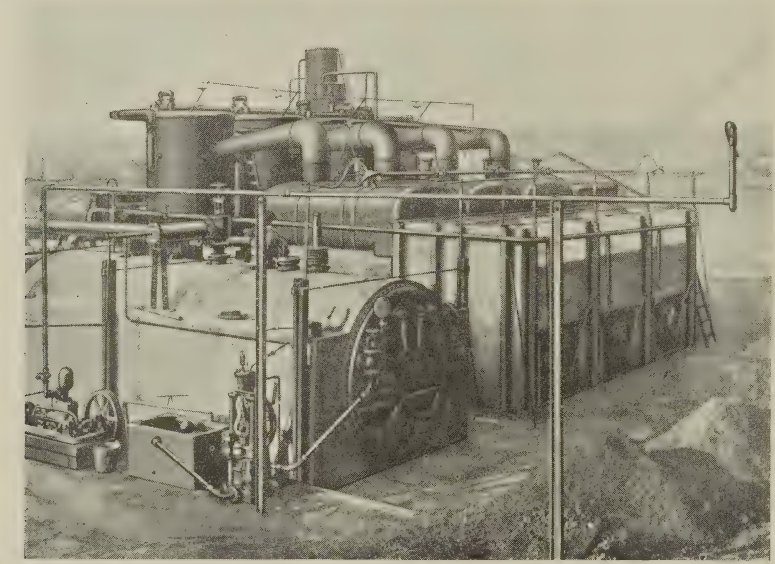

FIG. 67.—HIRD PLANT; 4 STILLS (COKE-FIRED).

A perforated steam pipe is fixed in the third still for steam distillation of anthracene, otherwise there are no obstructions in any of the stills. Arrangements are made for the separation of anthracene and naphthalene, and fractions containing these products are cooled either in half-round open top pans, or in rectangular covered tanks. The latter tanks are preferable in hot climates and particularly when cooling is effected by refrigeration.

Owing to the total absence of any obstructions in the still, there is no opportunity for the "free carbon" to accumulate, and consequently overheating of the

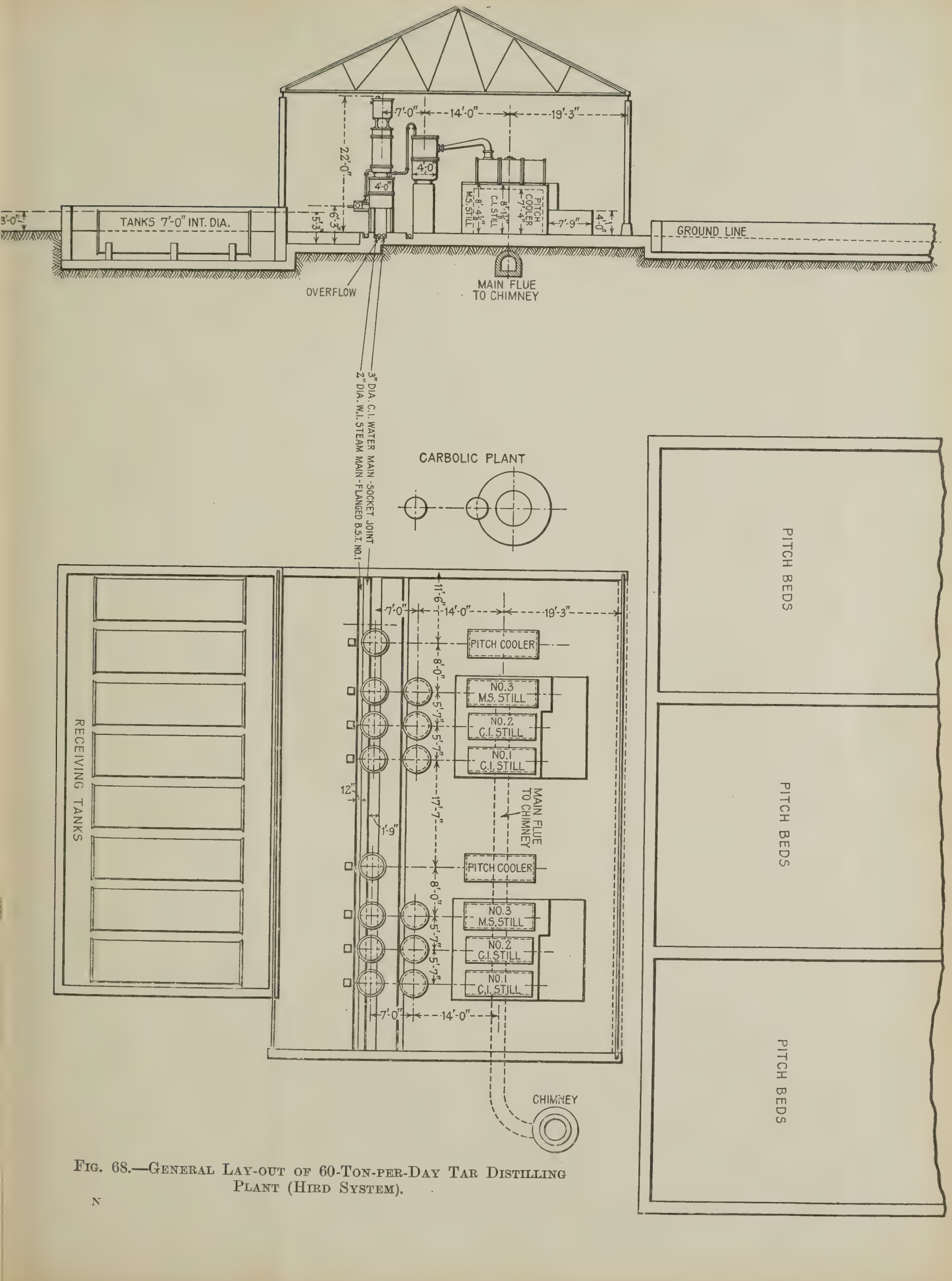

Fig. 68.—General Lay-out of 60-Ton-per-Day Tar Distilling Plant (Hird System).

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plates does not occur. For inspection purposes the front end plate of the still is bolted to the still, and may be conveniently removed when desired. The back end plate is welded to the still. All connections from one still to another are fixed outside at the front end of the stills. They are not submitted to the heat of the flue gases, hence there is no risk of carbonisation or blocking in these connections.

A plant when dealing with one ton of crude tar per hour gives the following figures :—

Pitch.	Delivery per hour		1,080 lbs. per hour.
Distillates.	No. 1 Still.	Crude naphtha	20 galls. ,,
	No. 2 Still.	Light oil and creosote	51 ,, ,,
	No. 3 Still.	Anthracene oil	30 ,, ,,

WORKING TEMPERATURES.

No. 1 Still.	210° C.
No. 2 Still.	260° C.
No. 3 Still.	260° C.

Steam consumed in No. 3 Still (for anthracene)	120 lbs. per hour.
Water used for condensing purposes	90 galls. per hour.
Temperature of pitch at outlet	150° C.
Temperature of ingoing tar	100° C.
Fuel consumption per ton of tar distilled	90 lbs. of coke.

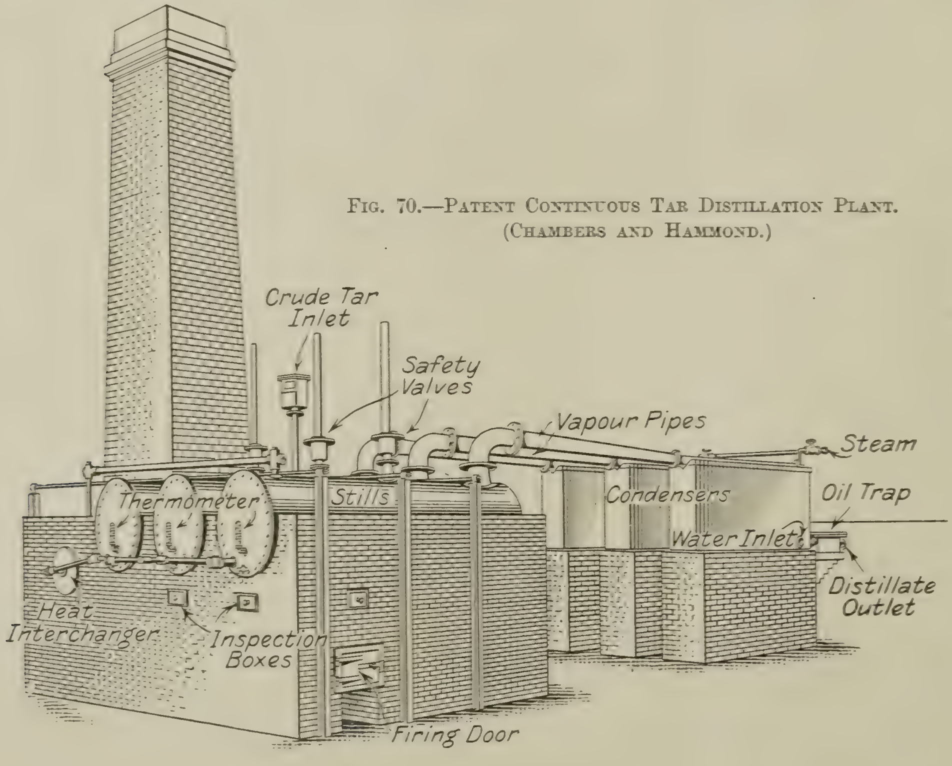
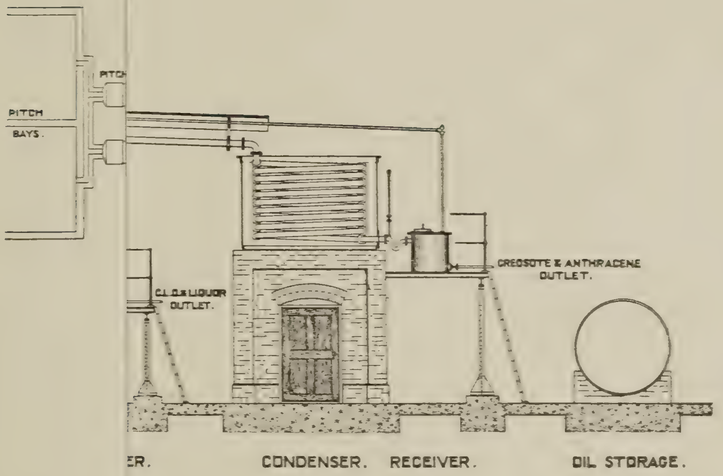


FIG. 70.—PATENT CONTINUOUS TAR DISTILLATION PLANT. (CHAMBERS AND HAMMOND.)



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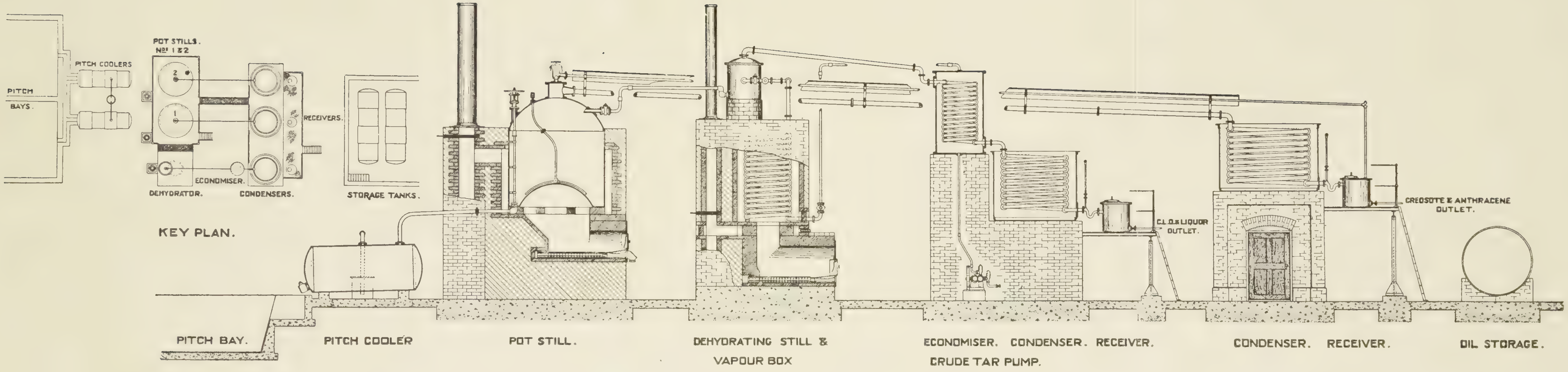

Fig. 69.—Wilton's Tar Distillation Plant.

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It will, no doubt, be observed that the working temperatures are extremely low, although the plant at the time the figures were obtained was producing pitch having a softening point of 60° C. Such low temperatures are a great advantage, enabling the maximum yield to be obtained from the tar, owing to a complete absence of carbonisation.

The low working temperatures are made possible because there is no local overheating in this type of still, owing to the rapid and unrestricted circulation of the tar.

It should be also stated that in this system distillation takes place at a very low pressure, the vapours passing through one condenser only of comparatively large diameter. This low working pressure again assists in maintaining a low temperature.

Plants of this type are at work on Mond producer gas tar, one unit dealing with 20 tons of tar per day. Although this tar contains between 30 per cent. and 40 per cent. of water, " priming " has never been experienced during a continuous running period of two years. The plant referred to is erected at the works of the South Staffordshire Mond Gas Power Company. Units are also at work distilling together 40 tons of tar per 24 hours.

The distillation of tar under vacuum is not a general practice in this country, owing chiefly to the higher initial outlay on the plant, and the greater risk of explosion should air by any chance leak into the still.

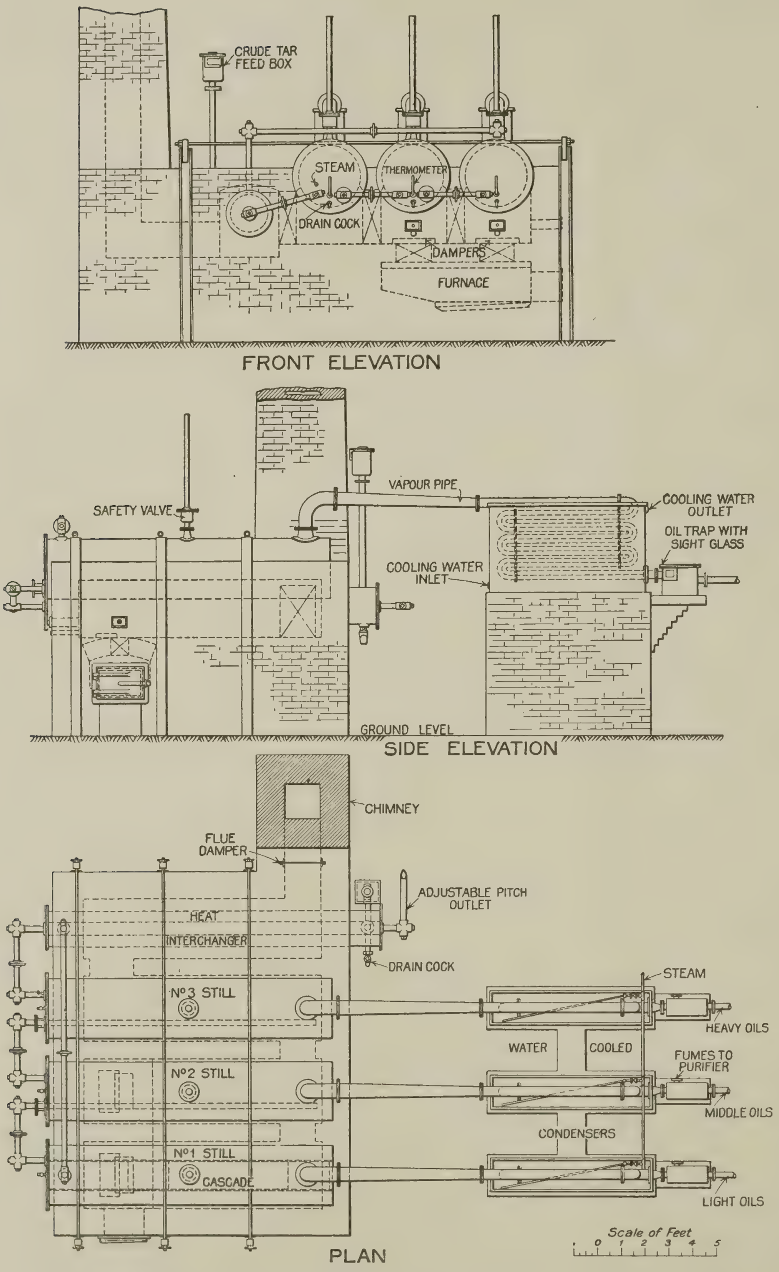

Fig. 71.—Patent Cascade Type Continuous Tar Distillation Plant. (Chambers and Hammond.)

CHAPTER IX

DISTILLATION OF COAL TAR

THE object of distilling coal tar is to increase its usefulness, and, therefore, its commercial value. Broadly considered, the process of distillation is the same in all works. It differs only in certain details, such as (*a*) the method of testing for the "cut" or "change-over point" for each fraction; (*b*) the number of fractions a certain tar will yield, or it is desired to collect; (*c*) the wish to manufacture special products from the fractions; (*d*) the quality of pitch required, and (*e*) whether it is required to make special preparations from partly distilled tar, and so on.

By far the largest portion of the tar which passes through a tar distillery is worked for benzoles, naphthas, creosotes, naphthalene, anthracene, carbolic, and cresylic acids, pyridine and pitch, and the distilling of a charge of tar for the various fractions from which these products are obtained, and for pitch, will receive attention before dealing with special preparations. It will be assumed that a preheater is connected to the tar still, and that both are empty.

A charge of tar is pumped into the preheater from the storage tank or well. It is desirable to work well-settled tar, as some of the entangled ammonia water will have separated to the top, and in consequence less time will be occupied in distilling off this material. While charging the preheater, the manlid of the still should be placed into position, the joint being made of lime putty; a mixture of slaked lime and water of the consistence of butter. The condensing worms, mains to the receivers, and safety devices should be inspected to see if they are clear of obstruction, *i.e.* not choked up with naphthalene or anthracene salts. A 15- to 20-ton preheater may be charged through a 6-inch main in between thirty and forty-five minutes.

The preheater having been properly charged, the supply is cut off, and the tar turned into the still. As soon as the preheater is empty, *the discharge cock is shut off*, and a fire or the producer gas ignited. A further charge of tar is pumped into the preheater at the same time by the stillman's mate. The heating up of the tar may be pushed until the swan neck becomes hot, but immediately that sign becomes evident considerable care must be exercised in order to avoid "priming" or boiling over of the tar. At that point, then, the fire is slackened a little, and the worm end watched for the first drops of the distillate. The distillation is now proceeded with, with caution, and it may become necessary to slacken the fire a little more at this stage. Sufficient heat must, of course, be supplied to keep the distillate flowing gently from the worm-end into the collecting box. Should "priming" unfortunately occur, damping the fire, or shutting off the gas, and playing or pouring cold water on the still top will soon stop it. It is not a bad plan to run a 1-inch emergency water main across the battery of stills, and place in it several cocks and connect these to short lengths of hose. The tar which comes over during "priming" should be turned into the overflow tar receiver, the openings from the collecting box to the dividing box being promptly shut.

This portion of the distilling operation is known as the crude naphtha stage, and the fraction consists of ammonia water and crude naphtha. During the whole time the fraction is passing the water in the condenser tank must be kept running, and the supply should be cold. The distillate drops from the worm-end into the collecting box and then passes into the divider, where the ammonia water sinks to the bottom, and is removed by the water pipe to the inspection box, then via the liquor main to the receiver. The crude naphtha flows through the outlet near the top of the divider into the main, which conducts it to the receiving tank. For a while the amount of water in the distillate exceeds that of oil, but as time goes on the amount of the former decreases—the latter, of course, increasing. At this stage the temperature may be increased a little, but it is yet necessary to continue careful firing. The flow of the liquor and naphtha into the receiver mains is regulated by raising or lowering the elbows, the one inside the inspection box and the other inside the divider, as explained on pages 154 and 155 respectively. As the amount of water in the distillate decreases, so *with care* may the temperature be raised, but not unduly rapidly. Towards the finish of this fraction the small quantity of water still coming over will change in colour from a greenish yellow to a blood-red. From now the stillman should collect occasional samples at the worm-end, allow the oil to separate, and take its specific gravity. When this reaches a figure prearranged by the works manager, the outlet to the divider is closed, and the cock on the light oil receiver main opened. This point is known in tar works terminology as the "change over," "cut," or "turn over," point. The specific gravity at the "turn over" point may vary between 0·950 and 0·965 at 60° F. Some stillmen "cut" the distillate when water ceases to come, but this method often results in a crude naphtha containing rather more heavy material than is desirable. The length of time required to work off this distillate will vary according to the state of the tar and the volume of the charge. With normal tar and a 15- to 20-ton charge, 6 to 12 hours may be taken as average times, and with reference to the yield of the distillate this may vary between 3 and $6\frac{1}{2}$ gallons per ton of tar. During the working off of this fraction the pull on the foul gas mains should be slight, otherwise there will be a loss of light products if a recovery plant is not attached to these mains.

The strength of the ammonia water from the fraction is generally between 2 and $3\frac{1}{2}$ per cent. of total NH_3, and this product is worked up at the tar distillery, or else sold to a firm of ammonia distillers. In order to avoid loss of ammonia, the receiver should be kept well sealed, and the liquor removed and dealt with as quickly as possible. Crude naphtha varies somewhat as regards specific gravity, but it usually ranges between 0·905 and 0·920. From it are obtained chiefly benzoles, toluoles, and a little light naphtha. Full details on the working up of this material are given in Chapters XII, XIII, XIV.

Soon after the " change over " to the light oil fraction, the distillate will begin to run from the worm-end in a moderately thick stream, and practically free from water. The temperature is gradually increased, in order to keep the distillate running at an even rate. At times, when partly through this fraction, some water comes over with the oil. It is not usually necessary, however, to slacken the firing, and the beginner should not be alarmed if this occurs. As the process continues, the amount of naphthalene salts in the distillate increases, and it is necessary to prevent this material from crystallising out and choking up the condensing coil. To do this, the flow of water through the condensing tank is stopped very shortly after the " cut " from crude naphtha is made. The water in the tank then becomes gradually hot by absorbing heat from the distillate as it passes through the condenser worm. Should the tar contain a large quantity of naphthalene "salts," making this fraction extremely "salty," it is advisable to bring the temperature of the water up more rapidly by introducing a little open steam into the condenser tank. Generally the water is allowed to get hot when the specific gravity of the distillate stands at between 0·970 and 0·990 at 60° F. The " change over " point from light oil to light creosote varies according to the nature of the tar, or if it is desired to make a distillate for a special purpose. On this account the stillman may " cut " the distillate when the oil running from the worm-end reaches a specific gravity between 1·010 and 1·030 at 60° F. The length of time taken to work off this distillate will vary, of course, according to the volume of the charge and the nature of the tar ; for a charge of 15 to 20 tons, 2½ to 8 hours may be taken as average figures. Yield per ton of tar is also chiefly affected by the nature of the tar, and may vary between 12 and 25 gallons. As a little more foul gas is given off during the working of this fraction, and its constituents are not so volatile as those of crude naphtha, it is advisable to increase slightly the pull on the foul gas main. The specific gravity of light oil may vary between 0·960 and 1·009 at 60° F.

As the distillation proceeds, the oil running from the worm-end begins to appear more or less yellow in colour, and the smell of sulphretted hydrogen, and other foul gases, gets a little stronger. A greater pull is put on the foul gas main, and more heat is applied to the tar. The temperature of the water in the condenser tank is kept elevated, as the distillate will still contain a fairly large quantity of naphthalene "salts." Frequently towards the end of this fraction the oil will show a tendency to set rapidly solid on cooling, due to a predominance of naphthalene "salts." This fraction is known as light creosote, middle oil, or carbolic oil, and, as the last name indicates, is one from which carbolic acid and its homologues are obtained. It is not the only one, however, as some tar acids are recovered from both the crude naphtha and light oil fractions. It is advisable to " cut " earlier for this fraction if the tar contains a large quantity of naphthalene. The point at which the distillate is " cut " to make this fraction varies between fairly wide limits, viz. when the specific gravity at the worm end stands between 1·035 and 1·055 at 60° F. and sometimes a little higher (1·060 at 60° F.). According to various conditions, the yield per ton of tar may be between 8 and 13 gallons, and the specific gravity will range between 1·030 and 1·045. The length of time taken to work off this fraction, say, from a 15- to 20-ton batch, falls between 1½ and 3½ hours.

As the process continues the distillate gets much yellower, the odour stronger and the tendency to set solid on cooling sometimes decreases. More pull is necessary on the foul gas mains, and heavier firing is required to keep the distillate flowing from the worm-end in a thick, continuous stream. It is advisable to keep the water in the condenser tank hot, in spite of the general tendency shown by this fraction to remain liquid at more or less normal temperatures ; sometimes it does not. To obtain what is known as the creosote or heavy creosote fraction, the distillate is " changed over " when the specific gravity at the worm-end is about 1·070 at 60° F. It is difficult to give definite figures for the yield of this fraction, or of the length of time it takes to work off ; they vary very much according to kind of tar worked, what is desired of the fraction, and so on. As a rough guide the yield may be taken as ranging between 28 and 35 gallons per ton of tar, and the time to work the fraction off a 15- to 20-ton batch, between 5 and 7 hours. The specific gravity may be within the limits of 1·050 and 1·065.

A stage in the process has now been reached in which the distillate has a very strong odour of sulphides, is of a greenish yellow colour, and as it flows from the worm-end in a thick stream appears viscid. This fraction contains anthracene " salts " and is liable to bring about an obstruction in the condensing worm, unless the temperature of the condenser water is high. It is advisable to keep the water at about boiling-point. After this fraction has been running for a short time, the fire is slackened and steam is introduced into the still. The introduction of steam helps to lengthen the life of the still bottom by reducing the tendency of the pitch to coke. It also reduces the time required for the distillation, and, if carefully managed, increases the yield of oil. The law of partial pressures no doubt plays a part in bringing about some of these results. Passage of steam into the still is continued until the finish of the distillation, which point is determined according to the quality of the pitch required. It is not possible to give a definite point at which to introduce the steam ; it will vary according to the quality of tar worked, and has to be found by experience. Roughly the introduction stage lies between the points at which the specific gravity of the distillate at the worm-end tests 1·075 and 1·090 at 60° F. Care must be taken to use perfectly dry steam ; wet steam, especially if inordinately wet, is liable to bring about a boil over. Slightly superheated steam can be used with advantage. A convenient pressure to employ is 70 lbs. to the square inch. The steam valve must be opened gradually ; steam must not be admitted into the still suddenly. It is advisable to let the fire die out, or shut off the gas, as the case may be, shortly before the finishing point is reached, the hot brickwork and the steam being sufficient to continue the distillation to the end. A still will continue to work for about half an hour to an hour after the fires are drawn, and if the precaution just mentioned is not taken, there is a risk of making the pitch too hard. According to the kind of tar being worked, or the quality of pitch required, the finishing point may vary between a specific gravity of 1·080 and

1·130 at 60° F. The yield of this fraction, known as anthracene oil or "green" oil, given approximately as a guide, may be between 3 and 18 gallons per ton of tar, and the specific gravity may range from 1·070 to 1·100 at 60° F.

When it is not desired to recover the anthracene, the heavy creosote and anthracene oil fractions are sometimes not separated but worked as one fraction. There are certain qualities of coal tar which yield so little anthracene oil that it is not worth while attempting to make a fraction. If it is desired to prepare a suitable creosote oil for burning in Wells or "Lucigen" lamps, then the heavy creosote distillate is "cut" at about 1·053 specific gravity at 60° F., and a fraction collected between this point and 1·075 specific gravity at the same temperature. A good burning creosote must be absolutely free from insoluble matter and suspended naphthalene "salts." It should commence to distil at about 200° C., and approximately 60 per cent. distil over by the time 260° C. is reached. The specific gravity may vary between 1·065 and 1·070 at 60° F.

In order that the stillman may test the distillate as it leaves the worm-end, he is provided with a No. 1 Twaddell hydrometer, a Fahrenheit thermometer with the scale inside (floating thermometers similar to those used in dairies are very suitable for the purpose), and some test jars. Tinned-iron test cans will prove more economical than glass test jars, which are easily broken. It is a good plan to arrange that the stillman has the "cut" or "change over" points given him at so many degrees Twaddell at 100° F. This facilitates matters, and minimises the risk of overrunning the points, as the time taken for cooling the sample is less than if a lower temperature were used; and it saves the man making a calculation in cases in which the distillate sets solid above 60° F.

If safety-valves are fitted to the stills, each of them should be examined and the valve given a twist on its seat to keep it in working order. This operation must be conducted while the stills are being charged, or before they commence to work. Syphon or U-pipes, if used instead of safety-valves, must be cleaned out and filled again with water before the distilling operation commences. A good method of cleaning these pieces of apparatus is to blow steam through them from a jet, which may be fixed in a convenient place on the top of the battery of stills. All the receiver mains should be blown out with steam immediately after the distillate has finished running through them, or at the latest soon after the distillation has ended. The mixture of condensed steam and oil which results from this process is collected in a small tank called a "slop tank," the contents of which are kept warm by a small closed steam coil and the water and oil separated from time to time. The oil can be mixed with the creosote distillate. It is very advisable to clean out the foul gas mains at least once a week, by blowing through them with open steam.

The residue in the still (pitch) is allowed to remain for a varying period before running into the cooler. This is necessary in order to minimise the risk of damage to the still and its brickwork settings owing to the great heat stored up in them, to put less strain upon the cooler should this be of metal, and to reduce to a minimum the danger of the pitch taking fire. How long a period should elapse before "running off" the pitch will depend upon circumstances; for instance, whether the coolers are built of iron plates, or of brick, or constructed on the French weir system. The quantity of pitch in the still is another factor in the case. As a good average time 2½ hours may be taken; but the author is acquainted with some cases in which 1½ hours is the full time allowed, and with others in which 6 or 7 hours are allowed to elapse before the running-off operation is carried out.

If the cooler is of the iron cylinder type, it must be prepared each time before running the pitch into it. Should it be fitted with a plug valve, the plug and seat must be cleaned and whitewashed. The plug must then be placed carefully on its seat, not jambed down too tight. Also the manhole should be covered properly with its lid, which may be lightly luted with lime putty. It is not necessary or advisable to fasten the lid down, for if it is left unfastened it will act as a kind of safety-valve. Sometimes the coolers are whitewashed on the inside, but this need not be done if they are arranged so that they drain well. Water must not be allowed to gain access to the cooler, as it may bring about trouble when hot pitch comes in contact with it. For this reason the manlid must be kept on during wet weather. Before releasing the pitch into the cooler, it is necessary to put a pull on the foul gas main. In hot weather it is a good plan to keep the outside of the cooler limewashed, if exposed to the sun's rays it will retard the absorption of heat, and so not hinder the cooling.

When discharging the pitch from the still, the cock on the tail pipe should be opened very gradually. If the pitch does not run, owing to its having set in the exposed portion of the tail pipe, and this sometimes occurs in very cold weather, then warm the pipe by placing under it a little tow soaked in creosote and igniting it. Care is necessary in carrying out this operation. A sufficient time must be allowed for the still to thoroughly drain. To completely drain the still lowers the works expenses, as it reduces the amount of pitch coke formed at each distillation, increases the number of times a still can be worked before cleaning, and minimises the amount of wear on the still bottom. It is not necessary, nor is it advisable, to remove the manlid of the still before discharging the pitch; nor need any of the connections be taken apart. The foul gas main connected to the coolers should be kept at work for between one and two hours after the pitch has been discharged into them.

After the still has been discharged, it must be allowed to stand empty for a period, the length of which will depend upon the size of the still and whether it is provided with a preheater or not. If there is no preheater, the flue dampers must be opened, in order to allow a current of air to pass round the still and cool it. After the lapse of between 1½ and 2 hours the still can be charged with cold tar. It is not advisable to shorten the time as this will introduce the risk of an explosion, and also bring about an undue strain on the rivets and seams, producing leaks. In cases in which a preheater is provided there is no need to draw the dampers, and the still may be charged again about half an hour after the pitch has been run off. The tar in the preheater being hot the danger of starting the seams, or of explosion, is avoided. Whether cold or hot tar is run into the still it is as well to commence the operation slowly, and increase the speed of flow, say, after about 5 or 10 minutes has elapsed. Before commencing the next distilling operation, it is as well to dip the still, to check the amount of the charge.

The pitch is allowed to remain a number of hours in the cooler before it is discharged on to the bay. It is not possible to give a definite time, as the size of the cooler, requirements of local by-laws, state of the weather, and other conditions will affect this. In any case, it is not advisable to run the pitch on to the bay too hot; some of the volatile matter is lost thereby, and acrid vapours are given off in such dense clouds that they create a nuisance. A good temperature at which to release the pitch is 130° C. When there are several coolers to discharge, it is best to release one of them at a time. Arrangements should be made to run the pitch on one portion of the bay only, by this method allowing a previous running to cool while another section is being dug. The pitch must not be run on to the bay too thickly: 12 to 18 inches is an ample depth, as much above this thickness will take an excessive time to cool, and is not dug so easily.

Before running off the pitch from the coolers the bay must be properly prepared to receive it. It is necessary to lime or chalkwash the bottom and the sides if these are of brick or concrete. Sand must not be used; the buyers do not appreciate it. The very thinnest wash of lime or chalk-milk is all that is necessary. Every endeavour must be made to keep water off the bay, at least just previous to the discharging operation and while it is going on. The effect of water on hot pitch is to fill it with vapour cells, or in other words to make it cellular, and this appearance is not sought after by buyers. There is, of course, the difficulty of coping with wet weather. The best plan to adopt on a wet day is to limewash the bay a few minutes before discharging the pitch, and then run it on to the bay as quickly as possible. If the pitch is run to the bay via a gutter, see that the gutter is limewashed and cleaned out after each operation.

After a still has been worked a number of times, varying according to the state of the tar, the care with which the still was set, and the amount of draining after each operation, it must be cleaned. A good average is seven times; often a still is cleaned after working four times, and cases occur in which it is not cleaned until it has worked eighteen times. The money and time spent in *frequent* still cleaning cannot be considered as wasted. It brings about a saving in fuel and increases the life of the still bottom, both to a considerable degree. In the cleaning operation, the mixture of partly coked pitch and "free carbon" must be cleaned or scaled off the still bottom and sides very thoroughly, taking care to remove any which may adhere to rivet heads or find lodgment in seams. The formation of this scale is due partly to the heat retained in the brickwork surrounding the still coking the thin layer of pitch left in the still at the end of the "running off" operation, and partly to "free carbon" which deposits and adheres to the bottom during the first and intermediate portions of the operation. For the scaling of stills, the following tools are in general use: short or miner's picks, straight and cross pane 4-lb. hammers and chipping chisels.

It is very necessary that certain precautions be taken to prevent accidents to workmen during the cleaning process. The still should be completely isolated from adjoining plant by disconnecting the swan neck from the condenser worm and the tail pipe from the pitch cooler. If there is not a small connecting pipe which can be removed completely, then a blank flange should be placed between the disconnected flanges. In cases in which the still is connected to a preheater the cock on the charge pipe must be locked or a blank flange used, as just described, on the still side of the cock. The manlid must be removed shortly after the pitch has been run off, and it is as well to drive out the foul air by blowing steam into the still. Sufficient time must be allowed for the still to cool before an entry is attempted. The length of time will vary according to the size of the still, the time of the year, and whether the still is one of a battery or the only one. It is best found by experience, but as a guide, 30 to 48 hours are general in tar-distilling practice. A responsible person should inspect the still before a workman is allowed to enter. The workman who enters the still must have a belt fastened round his body, with a rope attached. This belt is best made of stout webbing, and provided with two wash-leather pads on the spots which come under the armpits. In order that the wearer may be drawn up head-foremost in a case of "gassing," the belt must be worn well up to the armpits. Two men should be on duty outside the still, having charge of the free end of the rope and keeping watch on the workman inside for any signs of "gassing." The ladder which is used to descend into the still is provided with two right-angle hooks at the top, which fit over the manhole edge, and thus prevent slipping.

A new process for the distillation of tar has been introduced and patented[1] by the Barrett Company of New York. It consists in repeatedly circulating through the hot tar, contained in a still, an inert gas or a mixture of inert gases which will not condense at 0° C. at atmospheric pressure. Suitable gases are carbon dioxide and carbon monoxide, and if desired a mixture of these gases can be employed. The best results are obtained by passing repeatedly through the hot tar an amount of inert gas not less than one cubic foot per minute per 100 gallons of material filled into the still, and although not absolutely necessary it is desirable to heat the gas before passing it through the tar. In this process there is an increased yield of oil which becomes more pronounced the further the distillation is carried.

The following data are given in order to illustrate the results which may be obtained by using this process in the distillation of a coke-oven tar, and to make a comparison with the results obtained by known processes. The tar used had a "free carbon" content of 8·5 per cent., and in those cases in which gas was introduced it was passed at the rate of about 15 cubic feet per minute per 100 gallons of material charged into the still.

TABLE 56

	Per cent. by weight oil obtained.	Per cent. by weight pitch obtained.	Pitch, Air melting-point.	Pitch per cent. "free carbon."
Distillation without agitation	40·1	57·8	280° F.	40·7
Air used not recirculated .	33·0	63·0	286° F.	35·1
Nitrogen recirculated . .	52·0	46·4	277° F.	27·2
Carbon dioxide recirculated	51·2	46·7	270° F.	28·2
Mechanically stirred . .	40·0	57·9	300° F.	46·5

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[1] *E. P.*, 158,852. April 1st, 1920.

An advantage claimed by the inventors of this process is: That the distillation of a tar may be carried to such an extent that a pitch possessing a much higher melting point than one obtained by the usual method may be produced without endangering the still, and also a greater yield of liquid distillate results. It is considered that this is due to the small amount of carbon which is formed during the process; if a large amount of this material is produced there is a tendency to form coke on the still plates, especially on the bottom, with consequent burning, brickling or blistering of the plates due to poor heat transference from the fire to the still contents.

By the use of this process it is contended that pitches possessing melting points between 350° and 600° F. can be obtained without difficulty, or undue coking on the still plates, whereas by the ordinary methods of distillation it is not economically possible to obtain a pitch with a melting point above 320° F.

No mention is made by the inventors as to whether any difficulty occurs during the process of condensation due to the presence of non-condensable gas. It is a well-known fact that if there is present in a vapour to be condensed an appreciable amount of non-condensable gas, then the coefficient of heat transmission between the former and the condensing surface will suffer a very large decrease. This is due to the fact that a non-condensable gas exerts an insulating effect between the condensing surface and the vapour to be condensed owing to the property it possesses of attaching itself to the former.

Prepared and dehydrated tars are used for many purposes, the chief of which is for road treatment. Among the minor uses may be mentioned its employment in the manufacture of roofing felt, electric arc-lamp carbons, and the linings of converters used in the basic Bessemer process. Most of the specifications to which these prepared tars are made are the private property of interested firms.

Dehydrated tar is made without difficulty by carefully distilling off all the water (entangled ammoniacal liquor), and with it, of course, the crude naphtha, from a charge of coal tar. After these products have distilled off, the fire is drawn, the dampers opened, and the still allowed to rest for a few hours, when the dehydrated tar may be pumped into a storage tank, railway tank wagons, or filled into barrels. The connection between the still and the cooler must, of course, be broken, and the tail pipe of the still fitted up to a main connected to a pump, and also by-passed to a barrel-filling stand-pipe. Sometimes tar which has been kept in stock for a considerable time is called dehydrated tar, but in the strict sense this is not a correct term, as this kind of tar will contain a certain percentage of entangled water, in spite of long standing.

As already mentioned, by far the greater quantity of prepared tar is used for road treatment, and therefore chief consideration will be given to it in this connection. A batch of prepared tar, suitable for road treatment, may be manufactured as follows. Twenty tons of gas tar are charged into a still, and the ammoniacal water, crude naphtha, light oil, and middle oil distilled off, as described on pages 183–184. When the distillate at the worm end reaches a specific gravity of 1·045 at 60° F. the fires are drawn, or the gas shut off, and the dampers opened. The contents of the still are allowed to stand at rest until the temperature reaches about 250° F. and then 2300 gallons of heavy creosote of a specific gravity between 1·060 and 1·065 and free from " salts " and water, are added. Thorough agitation of the mixture is necessary. The creosote is added by pumping it through the tail pipe of the still, and agitation is brought about by blowing a gentle current of air into the still through the same pipe. A far better plan, and one which will not hold the still up while the half-finished material is cooling to 250° F., is to provide a cylindrical boiler tank of suitable size as a mixing tank, and run or pump the material from the still into this. It should, of course, be allowed to rest for an hour or two in the still before running into the mixing tank. This tank can be fitted with a mechanical agitator, or the agitation be carried out by blowing air into the material through a perforated pipe. After a thorough mixing, the prepared tar may be pumped into railway tanks or to a storage tank, or filled into barrels for despatch. As it is often required that the prepared tar be filled into tar-spraying machines hot, it is a good plan to place the storage tank in an elevated position, and provide it with a closed steam coil. By this means the tar can be run into the spraying machine by force of gravity, and hot. The specific gravity of prepared tars may vary between 1·16 and 1·125 at 60° F.

For quite a number of years there has been a considerable amount of discussion on the subject of tar preparations for road treatment. The Roads Board issued in April, 1911, a set of general directions and specifications relating to the tar treatment of roads, and these directions and specifications were revised in 1914. In 1916 these specifications were adopted provisionally as the British Standard Specifications for Tars and Pitches used for Road Work, and in 1923 the Ministry of Transport revised them.

The chief items in the tar specifications of interest to tar distillers are those which relate to : (*a*) the source of the tar ; (*b*) the specific gravity ; (*c*) freedom from water ; (*d*) fractionation ; (*e*) amount of phenols ; (*f*) " free carbon " content. Briefly, the specific gravity must be high, the amount of water and phenols soluble in water low, and the " free carbon " must not be higher than 20 to 21 per cent. If the reader desires further particulars he is referred to the literature on the subject, among which are the publications mentioned in the footnotes.[1]

The experience of practical tar distillers, which the writer can corroborate, shows that it is not possible for the tar distiller to produce from some crude tars a prepared tar that will answer the specifications laid down by the Roads Board ; and yet tars can be manufactured at these works which, when used on roads, give results equal to any that answer the Roads Board specifications. For example, the four tars A, B, C, and D in Table 57 have been used largely for road treatment, all of them giving excellent results, and yet when compared with the Roads Board specification only C and D answer it.

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[1] *General Directions and Specifications relating to the Tar Treatment of Roads.* H.M. Stationery Office, 1923, Price 1s. net.

" Improvements of Highways to meet Modern Condition of Traffic," by T. W. Smith. *Proc. Inst. C.E.*, series 1910–1911.

" Up-to-date Roads," by R. O. Wynne Roberts. *Trans. Soc. Eng.*, May, 1910, Vol. 1, No. 5.

" Investigations on Coal Tar and some of its Products," A. R. Warnes and W. B. Southerton, *Trans. Midland Junior Gas Association*, 1912.

TABLE 57

ROAD TARS

	Road Board Specification.	A tar.	B tar.	C tar.	D tar.
Below 170° C.	not more than 1 %	nil	¼ %	nil	nil
170–270° C.	not less than 16 % not more than 26 %	30 %	29 %	25 %	22 %
270–300° C.	not less than 3 % not more than 10 %	7 %	9 %	10 %	4 %

As a matter of fact A tar has been used on roads subjected to very heavy traffic and it has stood well for a period of two years.

It should be noted that gas tar as a road-binding material is now prohibited where roads drain into fishing waters. This is due to the fact that many complaints of fish poisoning have been received by the authorities. For other remarks on this subject see Chapter XXII.

There is no doubt that in the future tar distillers will have to devote more care and apply more technical skill in the manufacture of road tars if they intend to keep their business in these materials. Petroleum bitumen is becoming a very real competitor in this direction. Vertical retort tar is not a satisfactory material from which to prepare road tars, and the small quantity of " free carbon " present may be a contributory cause. It is quite possible, however, by the judicious addition of petroleum bitumen to produce satisfactory results. The presence of a certain amount of " free carbon " seems to be necessary in road tars, but exactly where to draw the line has not yet been determined with any degree of accuracy.

Some manufacturers of road tars advocate the addition of crude naphtha to these preparations. This should not be tolerated, as crude naphtha is a valuable benzole, toluole, and naphtha-yielding material. If ever middle oils are employed in the manufacture of road tars they should be deprived of the useful phenols first.

The author is strongly against the use of light tar oils and even middle oils in the process of " cutting back," not only on account of the value of these oils in other directions, but because of the great risk of producing coagulation and consequent precipitation of the suspensoid matters contained in the highly viscid prepared tars. It is well known that oils of a low-distilling range bring about this coagulation with great ease, and even with the oils of high-distilling range, such as heavy creosote and anthracene oil, it is necessary to use care and not to overstep the amount which can be safely used.

A prepared tar containing flocculated suspensoids is practically useless as a binding agent, as, on applying to a road the precipitated solid matter will be filtered out more or less by the external surface and left thereon, whilst the fluid oils will penetrate into the road substance simply " wetting " it, but in no way binding it, as a good prepared tar should.

The suspended matter in tar, when coagulated, is known by the appellation "free carbon," and although condemned by many as a deleterious or even useless ingredient of road tars, has been found by the careful and observant practical man to be of considerable value in a road binder, acting as a toughener and rendering the treated road less susceptible to climatic changes. The author's experience in the manufacture of road tars and in the results obtained from them leave no doubt in his mind as to the truth of these statements.[1]

That the actinic rays of sunlight when acting upon bituminous materials and on coal tar and allied products causes chemical and physical changes to take place with the production of " free carbon " is proved by much experimental evidence, but whether the amount formed by this means in, say, a road tar, plays a serious part in its disintegration, is very doubtful. In the author's experience he finds that water-gas pitch and materials containing this substance are affected by actinic rays to a much greater extent than coal tar or coal tar pitch. For fuller particulars the reader should consult the literature referred to in the footnotes ([2]), ([3]), and ([4]).

A tar for the manufacture of roofing felt may be prepared by distilling a charge of coal tar until the distillate at the worm-end tests 1·050 at 60° F. The distillate which comes over before this point is reached is separated into the usual fractions as already described. The residue is allowed to cool to about 240° F., either in the still or in a suitable mixing tank, and then mixed with creosote of a specific gravity 1·045 at 60° F., in the proportion of 1750 gallons for every 15 tons of tar distilled.

The process of continuous dehydration and continuous distillation of tar as carried out when using the Hird plants, described in Chapter VIII, will now receive attention. In the continuous dehydration plant the following takes place. On leaving the storage tank the crude tar enters the condenser tank by the tar inlet at the bottom, and in passing upwards to the outlet on the opposite side of the tank circulates round the condenser coil and absorbs heat from the distillate which is passing through this coil on its way to the distillate receiver. After leaving the condenser tank the crude tar passes through the inner tubes of the cooler, and while doing this it absorbs heat and cools the prepared tar which is flowing through the cooler jacket on its way to the prepared tar receiver. From the cooler the hot crude tar enters the still at a temperature approximating 70° C., and travels first down one side and then up the other, due to the presence of the longitudinal baffles. While the tar is passing through the still it is heated by means of the tubes at the still bottom, and it gives off in the form of vapour the water, the crude naphtha and light oils, which pass forward through the swan neck and vapour pipe to the condenser coil, where they are condensed, and from which they are conducted in the liquid form to the distillate receiver. The tar leaves the still, passes into the jacket of the heater, and thence into the prepared tar receiver.

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[1] *Trans. Midland Junior Gas Association*, 1912, pp. 108–109. See also " Investigations on Coal Tar and some of its Products," Arthur R. Warnes and W. B. Southerton.

[2] " Effect of Exposure on Tar Products," Chas. S. Reeve and Benjamin A. Anderton, U.S.A. Office of Public Roads and Rural Engineering, *Gas World*, October 28th, 1916, pp. 384–386.

[3] *Asphalts and Allied Substances*, Abraham.

[4] " A cause of Weakness in films of Bitumen Paints," A. R. Warnes, *Oil and Colour Trades Jour.*, May 4th, 1918, p. 1489.

The continuous process of tar dehydration offers several advantages over the intermittent system, among which are (1) low supervision charges, (2) low fuel consumption per ton of tar distilled, (3) reduced wear and tear of plant, (4) small area occupied by plant, (5) low cost of plant. Continuous dehydration plants can be arranged for the removal of the benzole and toluole which are taken up by the oil in the gas-washing. They are also very suitable for the preparation of prepared tars to answer the Roads Board specifications. It is, of course, necessary to vary the working temperature according to the kind of prepared tar required. For tar to answer specification No. 1 for spraying, the working temperature approximates 230° C., for specification No. 2, tar for macadam, a working temperature of 260° C. is necessary, and for specification No. 3, tar for grouting, a temperature of 288° C. is the best to employ. Naturally the character of the prepared tar and the yield of distillates will vary a little according to the quality of the crude tar passing through the plant.

Compared with the intermittent system, Hird's continuous system of tar distillation shows several advantages. The chief of these are :—

1. When started the plant is able to do its work automatically without depending entirely upon personal supervision.
2. Very low temperatures prevail throughout the whole of the stills, with the result that wear and tear of plant is reduced to a minimum.
3. The process being continuous, there is no loss of heat from stopping and restarting, and, consequently, there is a distinct economy in the cost of distillation.
4. The various fractions are automatically and simultaneously discharged into the receivers, and no attention whatever is necessary.
5. A plant to deal continuously with one ton of tar per hour never contains more than three tons of tar in process of distillation.

Briefly, the method of working this plant is as follows : The crude tar is conducted from the storage tank into the regulating tank ; from this tank it flows to the steam preheater, then to the first of the series of heaters, a constant head being maintained by means of a float valve in the regulating tank. In passing through these heaters the temperature of the tar is raised by its receiving heat from the distillates leaving the stills as they pass through the coils. During its passage the tar is deprived of practically all of its water and crude naphtha. The vapours of these materials pass into a common main, and thence through the tube of a coil condenser, in which they are condensed. The condensed liquids pass through a sight box and a separator, and then to their respective receivers.

After its passage through the heater-coolers the tar flows through the coil in the pitch cooler, and while doing this its temperature is further raised, while that of the pitch is correspondingly lowered. On leaving the pitch cooler the temperature of the tar may be from 120° to 200° C., according to the original composition. If the original water content has been high much of the heat will have gone into the removal of water during the passage through the heaters.

The tar is now distilled for its light oil, creosotes, etc., by adjusting the heating of the stills so that as the tar flows through them in succession it shows such temperatures as have previously been found to give desirable oil fractions. The anthracene distillation is helped by live steam as usual in tar distilling.

The residue from the last still is liquid pitch, and this passes from the still into the pitch cooler, through which it travels on its way to the pitch bay, and during its progress it gives up much of its heat to the crude tar passing through a pipe immersed in it, on its way to No. 1 still. The temperature of the pitch on leaving the cooler is such that it does away with the giving off of the irritating fumes so often observed when running off pitch in the intermittent system.

With this plant it is possible to adjust the temperatures so as to obtain continuously uniform fractions of any desired boiling-point, while at the same time the pitch can be varied to meet any desired twisting-point. One man is able to superintend the working of the plant, his duty being merely to adjust the burners and read the pyrometers, which indicate clearly the working of the stills.

As a tar-distilling plant, the principal commercial advantages are the heat economy rendered possible by continuous working, and the fact that the steel tubes employed as heating surfaces are a standard article, easily removed and replaced by a works fitter. This latter fact, set against the cost of boiler plate-work required on a steel still bottom of the vertical or horizontal type, represents a distinct advantage. Moreover, the main fabric of the still being of C.I. is practically indestructible and renewal of tubes does not require destruction of brickwork or the disturbance of the still itself.

It is now possible to estimate and guarantee the probable life of a tube on various types of tars, as a wide experience of the effects of different tars has been obtained.

The Hird Plant is particularly attractive to coke-oven installations, because the tar production at such places is generally on a scale where complete distillation is directly profitable ; surplus gas is available for firing, and the works is guaranteed an ample supply of fresh wash-oils, blended according to the exact requirements of the benzole plant.

The most noteworthy recent installations have been one set of thirty tons per day capacity, being the second repeat order from the Team By-Product Coke Co., near Newcastle-on-Tyne, and the complete installation at the Rother Vale Coke-oven Plant, near Rotherham, capacity sixty tons per day. (The latter is shown in illustration, Fig. 68.) Both these are gas-fired plants.

To enable the works manager to keep some sort of check on the yield of the various distillates obtained from the tar which he is passing through his stills from month to month, it is a good plan to make out a balance-sheet, say, once a week, similar to the following :—

	Tons.		Gals. per ton.	Tons.
Tar distilled	100	Liquor	5·86	3·00
		Crude naphtha	3·83	1·56
		Light oil	16·80	7·57
		Middle oil	9·68	4·47
		Creosote	29·40	13·72
		Pitch	—	67·78
		Loss (by difference)	—	1·90
	100			100·00

ULTIMATE PRODUCTS

Benzole, 90 per cent.		1·71 galls. per ton tar.
Solvent naphtha, 90–160°		2·06 ,, ,, ,,
Heavy naphtha, ·920°		0·45 ,, ,, ,,
Carbolic, 50°		4·03 ,, ,, ,,
Creosote—		
From tar direct	39·08	
From bottoms	14·39	
		53·47 ,, ,, ,,
Pitch		13·55 cwts. ,, ,,

Working costs in regard to the distillation of tar will vary in different works according to local conditions, kind of tar, type of plant, condition of plant, whether gas or coal firing is employed, and so on. The following figures may, however, prove of some use as a guide to beginners :—

Wages productive and non-productive, 2s. 6d. per ton of tar distilled. Stillman's wages, 4½d. per ton of tar distilled. These are pre-war figures, and in order to obtain the correct ones it will be necessary to add to them the percentage increase in wages, etc., existing at the present moment.

As there has been, and still is, a considerable amount of discussion on the subject of fish poisoning due to the drainage of tarred roads running into fish ponds and streams, the author thinks it advisable to call the attention of readers to a paper entitled, "A Note on the Determination of Tar Acids in Drainage from Tarred Roads," by J. J. Fox and J. H. Gauge.[1]

Further, in connection with this subject, the reader is referred to a short notice upon the alleged destruction of trout by coal tar, which appeared in the *Gas World*.[2] An interim report has been recently presented by a Joint Departmental Committee appointed by the Ministries of Transport and of Agriculture, after it had considered the question of damage to fisheries by pollution caused by rain washings from tarred roads. The conclusions reached by this committee are :—

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[1] *Jour. Soc. Chem. Ind.*, Vol. 39, No. 15, p. 260T.

[2] July 17th, 1920, p. 55.

1. That rain-washings from a water-bound granite road surface are not in ordinary circumstances injurious to fish or fish food.

2. That the first rain-washings from such a surface which has been recently tarred (say, within a week) will certainly be injurious, to fish and fish food, unless mixed with at least an equal volume of unpolluted water, and may be injurious unless mixed with a considerably larger volume of unpolluted water. That they will not, however, be injurious to fish or fish food if diluted with at least ten times their volume of unpolluted water.

3. That subsequent rain-washings from such a tarred road in the early stages of its life are not injurious to fish and fish food, provided they are mixed with at least an equal volume of unpolluted water.

4. That filtration through freshly cut turf reduces to an extent not yet precisely ascertained the injurious character of rain-washings from such a tarred road.

5. That storage of rain-washings from such a tarred road reduces in some respects their toxic character.

6. That while pond vegetation appears to be uninjured by rain-washings from such a tarred road of which the surface is unbroken, washings carrying silt from such a tarred surface which is breaking up damage watercress.

7. That rain-washings from such a tarred road in process of disintegration will certainly be injurious to fish and fish food, unless previously mixed with unpolluted water to an extent not yet ascertained.

These conclusions apply when the tar used complies, except in respect of excess of naphthalene, with the Roads Board Specification for Tar No. 1. It should be noted that the experimental work was carried out at Alresford, Hampshire, at a point where the rain-washings from a stretch of main road in the open country could be passed into small ponds stocked with trout, and furnished with a sufficient supply of natural food and flow of good water to maintain the trout in health when the water supply was uncontaminated by road-washings or other specific pollution. The committee suggested that highway authorities should give preference to asphaltic bitumen free from tar products for the treatment of roads draining directly into fishing waters.

In the author's opinion this report is not altogether convincing from the practical point of view. Apparently the small ponds were made specially by the road side; rather an unusual place for fish ponds. In cases where almost stagnant fishing waters are near to roads, a field or a portion of one intervenes, and the drainings from the roads would have to percolate through some yards of soil before they reached the water. It is very questionable under these circumstances whether they would be dangerous. The obvious remedy in risky cases is to prevent the drainings from running into the pond. In regard to running streams in proximity to roads, these are usually separated by a bank or narrow width of land, and unless the drainings are deliberately run into the stream the element of danger is absent. Even in cases in which the stream is *immediately* alongside the road (if such do exist), considerable dilution of the road drainings would take place almost at once, and thus destroy the injurious nature of the polluted water. The speed of the flow of water in the experimental ponds is not stated.

If the tar used on a road has been prepared according to the Roads Board Specifications it should not, " on vigorous agitation for a quarter of an hour, with twenty times its volume of water at 21° C. impart to the water more than 5 grains of phenoloid bodies, reckoned as phenols, per gallon of water (0·007 per cent.)." This is a very small quantity, but it is quite sufficient to act destructively on fish life. Wynter Blyth states that a solution of phenol in water of 1 : 7,000 kills dace, minnows, roach, and gold fish, whilst 1 : 100,000 appears to affect the health of fish. The amount of phenoloids in the washings from Roads Board tar (obtained as per directions given above), viz. 0·007 per cent., represents 1 : 14,286, and in order to reduce the strength to well below the danger figure dilution with, say, eight times its volume of water is necessary. Now, it is quite unlikely that even a very heavy downpour of rain on a freshly tarred road will yield washings containing 0·007 per cent. of tar acids; the vigorous shaking and the same ratio of tar to water would not exist, and a very considerable portion of the tar with its tar acids, etc., would be bound by the road material, say, by adsorption, *especially if the road has been properly prepared before tarring.* If we consider a downpour of rain of 0·2 inch on a portion of a road 30 feet wide and 200 feet stretch, *well prepared and properly tarred,* the amount of water to drain off that portion will be, in round figures, 623 gallons. The average content of phenoloid bodies in this water is not likely to exceed 0·002 per cent., or 1 : 50,000, and dilution with $1\frac{1}{4}$ times its volume of unpolluted water will destroy its dangerous nature. If the road is built with a proper camber then, approximately, only one-half of the volume of drainings (311 gallons) will fall towards the stream alongside the road.

How can silt from a tarred road surface get into a pond unless the drainings carrying that silt are deliberately discharged therein, or the edge of the pond forms one side of the tarred road ? Watercress can be damaged, not only by " tarred road silt," but by any material which will adhere to the floating leaves and thus choke the stomata.

The author doubts the usual opinion that the phenols in the surface drainings from a tarred road are the sole cause of trouble, *when it occurs.* Is it not likely that one or more of the auxetics which occur in tar (say, acridine) may contribute towards the poisonous nature of undiluted washings ? Acridine is sparingly soluble in cold water, and even very dilute solutions of it cause intense irritation when applied to the mucous membranes ; and fish are very sensitive creatures where irritant poisons are concerned.

APPENDIX 1

In a paper on low-temperature carbonisation given by J. Stanley Morgan, M.Sc., before the Coke Oven Managers' Association, Durham, on March 24th, 1923, a new method of carbonising coal by the use of a lead bath was discussed. The chief point about this method, which is of interest to tar distillers, is the fact that a tar is obtained which yields approximately only 30 per cent. of pitch, which requires less working up than any other type of tar, being even easier to handle than vertical retort gas tar. It is worthy of note that the oils from this tar are said to contain no benzoles. Mr. Morgan also stated that the lead bath had been successfully applied on a large scale to the distillation of coal tar oil.[1]

APPENDIX 2

H. M. Lowe[2] points out that tar distillation from pot stills, as practised generally, is thermally very inefficient, and that at least four times the theoretical quantity of fuel is used. He goes on to say that "The main fuel saving will be made by reconsidering in detail the design of the stills and flues, and a successful solution of this problem would do much more than is possible by a preheater. Secondly, self-cooling of the pitch in the still by the passage of steam or other inert gas should help considerably, and if developed do away with the necessity for pitch coolers. Thirdly, it has been shown that preheaters, apart from their main purpose of utilising the heat of the oil vapours, are justified."

Whilst this writer is correct in most of his assertions, the author thinks that the best method of reducing the consumption of fuel used for the distillation of tar is to carefully study the process of continuous distillation, and improve upon existing continuous plants rather than concentrate attention on modifying the design of pot still flues and settings. It is not possible to design flues for pot stills which will give results anything near the theoretical. One thing which stands in the way is the expansion and contraction which takes place in the still itself, which creates a considerable amount of leakage between the brickwork of the flues and the still; another, that the smaller type of pot still hardly lends itself to being set in a divided flue; another, that with certain types of tar a curtain arch or other protection for the bottom becomes necessary.

Self-cooling of the pitch in the still by the use of steam or inert gas is not the best plan; it is better to transfer the heat of the pitch to cold tar.

It has been suggested to the author that heating a tar still by means of oil baths (heating by oil circulation) will make for economy so far as fuel consumption is concerned. No doubt there is a great deal in this, but it seems that if the product itself, *i.e.* the tar, can be used to a very great extent as the "oil bath," thus considerably minimising the amount of fuel which is necessary to heat up a portion of the tar initially, then a very substantial economy is secured in the process of tar distillation.

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[1] Messrs. Woodall, Duckham and Jones, Ltd., London, have formed a research committee to exploit the lead bath process.

[2] "The Theoretical Heat balance of Tar Distillation," the *Gas World*, Coking Section, January 6th, 1923, p. 14.

A process which appeals very much to the author, and which uses this method, is that invented by Messrs. Major and Co., Ltd.[1] A brief description of this process is as follows, and the plant used is illustrated in Fig. 72.

Major's continuous distillation plant is the result of a number of years' experimentation, and at the present moment there are several plants installed which are doing all that is claimed for them. In addition to the distillation of crude tar to pitch and the manufacture of road tars, this plant can be used for the continuous distillation of crude petroleum, light oils, etc. One advantage of Major's system is that a battery of intermittent stills of the usual pot type can be easily adapted with little alterations to existing fittings, pipe lines, or connections. Tars with a high content of water are easily worked without the risk of priming, and the products obtained are of excellent quality. The system is easily understood when reference is made to the diagram, Fig. 72. From the store tank the tar is pumped to an overhead tank fitted with an arrangement so that a constant head is maintained on the feed to the distillation plant. This feed passes first of all through preheaters, similar to those attached to the usual intermittent plants, where the crude tar acts as a partial condenser for the vapours from the stills. After leaving the preheaters the crude tar passes through the pitch cooler by means of a series of pipes (where further heat is extracted from the pitch and the tar gains in temperature), and then to an overhead vapour vessel where any light vapours distil off. From this vessel the crude tar passes to the first still which is fitted internally as shown in Fig. 72, and it is led by means of a pipe to the bottom of the still. It then ascends the vertical tubes, which are surmounted by trays with serrated edges. In its course through the down pipe and vertical pipes the crude tar is heated by the material (tar) in the still, which serves as a bath. At the trays vapours are given off and the heavier undistilled portion of the tar flows over the serrated edges of the trays into the body of the still. The overflow from this still is taken from the bottom so that the material must pass through the whole of this vessel before running to the next still.

The stills are maintained at definite temperatures to fix the fractions and residues, and by control of these temperatures and coil-end tests any desired residue such as prepared tar or pitch of a definite test can be obtained, also the fractions can be controlled to any desired degree. It is important to note that the internal fittings are made in sections, and are easily removed for cleaning purposes.

As an example of the efficiency of this system, a battery of three or four stills (according to the nature of the crude tar), each holding about 800 gallons, can work 100 tons per day of 24 hours of crude tar to pitch. At the Wolverhampton works of Messrs. Major and Co., Ltd., a run of 9,000 tons of tar through a battery of three stills, to prepared tar, gave most satisfactory results and no cleaning was required ; the still plates being absolutely clean on examination after the passage of this large quantity of tar.

The system shows an excellent thermal efficiency, and the patentees secure further saving by the installation of a waste heat boiler in the flues, which can be made to supply steam for part of the process or for pumping.

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[1] Major's Continuous Stills. B. Pat. Nos. 13,572/1922 and 18,807/1922 (Cognate Still).

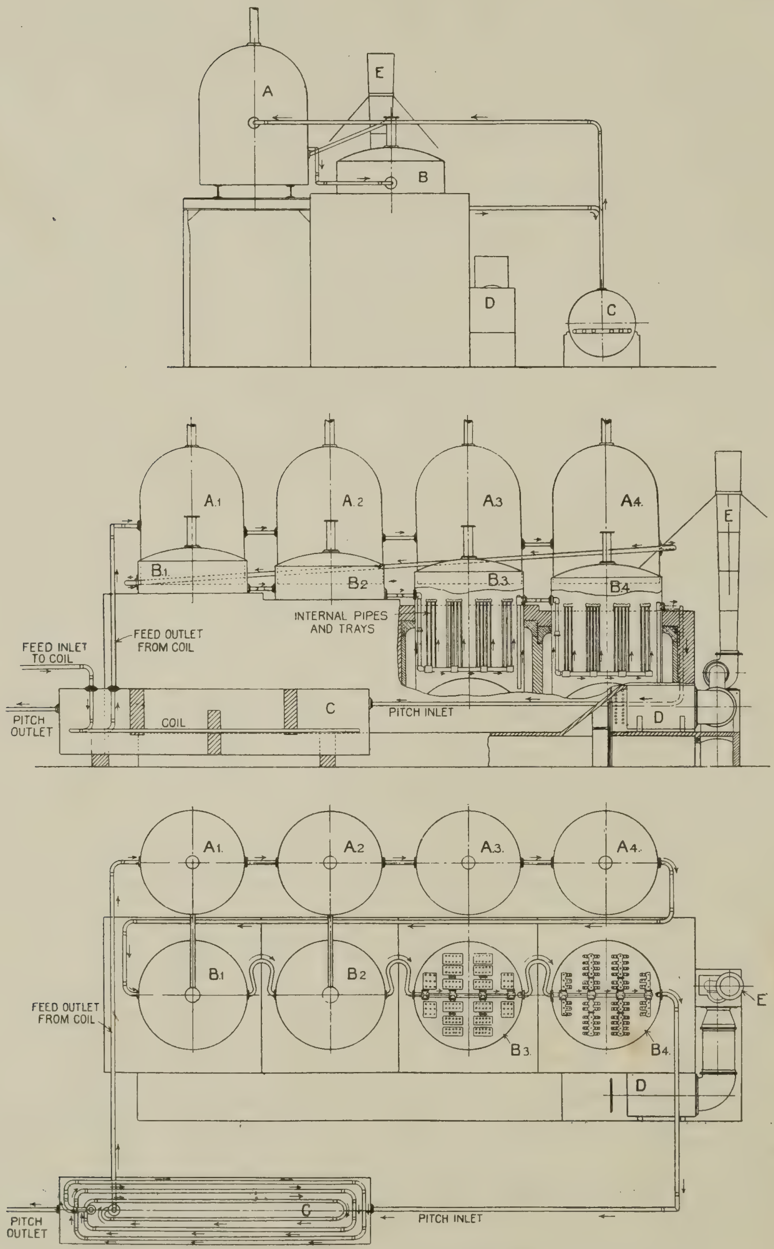


FIG. 72.—MAJOR'S PATENT CONTINUOUS SYSTEM FOR DISTILLATION.

A. Preheater. B. Still. C. Cooler.
D. Waste-heat Boiler. E. Chimney.

CHAPTER X

PLANT FOR RECOVERING CARBOLIC AND CRESYLIC ACIDS FROM OILS

THERE are two methods in general use for the recovering of phenols from tar distillates : (*a*) The sulphuric acid process, in which moderately dilute sulphuric acid is used to decompose the solution of phenolates—known technically as "carbolate" and "cresylate"—and the resulting sodium sulphate run to the drain, the phenols only being recovered ; and (*b*) the CO_2 process, in which carbonic acid gas is employed to decompose the "carbolate" or "cresylate," the resulting sodium carbonate being converted into caustic soda by causticisation, and used for extracting a further quantity of tar acids. The latter process is sometimes known as the "continuous process." It is much more economical to work than the former, although the initial outlay for plant is somewhat greater.

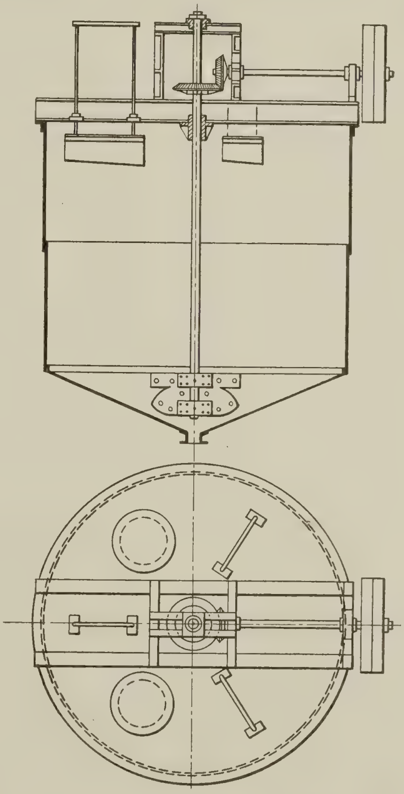


FIG. 73.—TYPHOON WASHER.

Washing tanks, generally known as washers, are required for both processes. These tanks may have a total capacity of 3,500 to 4,500 gallons, and in shape are generally cylindrical ; sometimes round-bottomed, trough-shaped tanks are used. The cylindrical washers are placed in a horizontal or vertical position. If in the former position, the washer should be tilted a little towards the outlet, but if in the latter, it should be provided with a dish or shallow cone-shaped bottom. A cone-shaped bottom will give the best results as regards draining. Horizontal washers are provided with a shaft on which are fitted agitating arms, and the journals of which pass through stuffing boxes let in each end of the washer. Good second-hand boilers, from which the tubes have been drawn and the ends blanked, make excellent washers. Vertical washers may be fitted with an archimedean screw agitator, or wing agitators, on a horizontal or vertical shaft. If an agitator of the latter type is used in the vertical position it is advisable to fit several fixed arms on the side of the apparatus. It is policy to cover the vertical and also the horizontal trough-shaped washers, and a manhole and lid must be provided.

In Figures 73, 74, 75, 76, will be seen diagrammatic illustrations of efficient types of washers suitable for use in connection with a tar acid plant. A washer of the Typhoon type is illustrated in Fig. 73, and it will be seen that it consists chiefly of a cylindrical tank with a cone-shaped bottom, a central vertical shaft suspended by a bracket at the top and having fixed at the bottom a small paddle, and three baffle plates which can be raised or lowered as desired. The motion of the paddle causes a vortex to form in the centre of the liquid contents of the washer, and the baffles which are placed in a position so that their bottom edges are just below the surface of the revolving liquid cause it to fall into the centre of the vortex. In Fig. 74 is illustrated a washer of the archimedean screw type as manufactured by Messrs. W. Neill and Sons, Ltd., and another type of washer manufactured by the

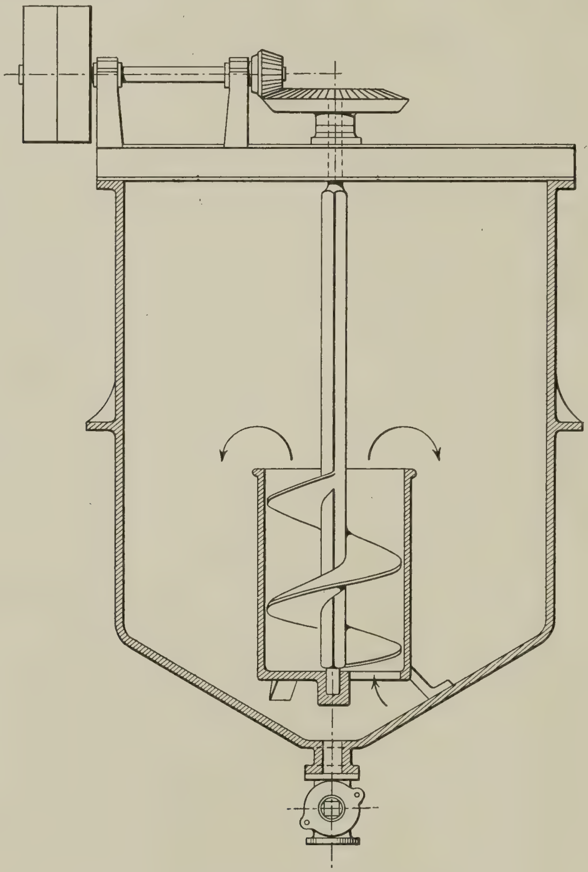


Fig. 74.—Washer by Neill and Son, Ltd.

Leeds and Bradford Boiler Company is shown in Fig. 75. The principle upon which these two types of washers act is easily seen from an inspection of the diagrams.

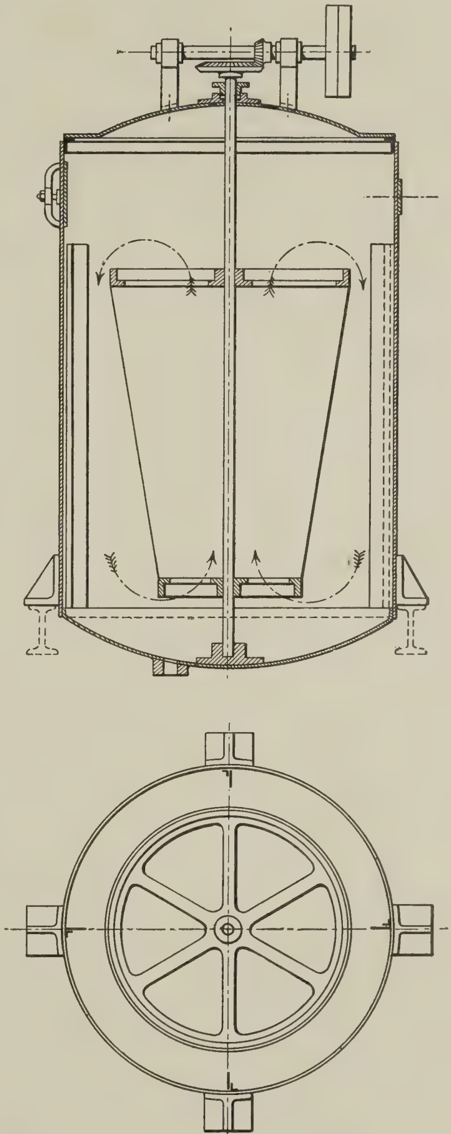


FIG. 75.—WASHER BY LEEDS AND BRADFORD BOILER CO., LTD.

A vortex mixer suitable for washing benzoles, naphthas, and also anthracene is shown in Fig. 76. It is made by Messrs. S. H. Johnson and Co., Ltd., and its mode of action is, briefly, as follows : A rotating vane near the bottom of the mixer imparts to its contents a rotary motion in a horizontal direction. Fixed curve plates near the top of the mixer continuously deflect the upper layer of the rotating liquid to the centre where the conflux of the streams from the several deflecting plates causes a considerable vortex, down which the liquid descends to feed the vane at the bottom, where it is again thrown out to the sides of the mixer. There is thus a rapid and continuous vertical circulation in addition to the usual horizontal swirling. This twofold motion of the liquid in the mixer causes a violent agitation which results in the most intimate and uniform mixing in a very short time.

A useful piece of apparatus to employ in connection with the washer is an oil separator. This is similar in pattern to the divider box described on page 154, Fig. 49, but it is often made a little larger. The object of using this piece of apparatus is to separate any oil from the final runnings and drainings of "carbolate" or "cresylate," a matter of some importance. Any oil which may come with the ammoniacal liquor, which it is sometimes necessary to draw off before commencing a wash, may be recovered if a separator is used.

With the exception of "carbolate" and "cresylate" storage tanks and tar acid storage tanks, which may be of any shape and size to suit circumstances, a "springing" tank is the only other piece of plant required in the sulphuric acid process. The "springing tank" may be constructed of wrought-iron plate, but even if care is used in conducting the process, some corrosion of the plates, and, if mechanical agitators are fitted to the tank, of the agitators, will take place. Lead-lined iron or wooden vessels are more suitable for this part of the process. It is now possible to obtain iron vessels homogeneously coated with lead, covered, and provided with an agitator. A vessel of this kind is very suitable for the "springing" of carbolate. Covered tanks provided with mechanical agitators are safer to use than uncovered tanks, the contents of which are agitated by hand. Wooden agitators are usually employed for hand agitation. The shape of a "springing" tank may be cylindrical, or like a round-bottomed trough, and cylindrical tanks may be placed horizontally or vertically. If in the latter position, and this is really the best, a dished or cone bottom should be fitted to the tank. This will allow of a better draining of the tank from the sodium sulphate liquor which separates after "springing." The cock fitted to the bottom of the tank to run off the contents should be made of acid-resisting metal, such as regulus metal or "Tantiron," for preference. Some workers prefer to skim the tar acids off the surface of the sulphate liquor, but this is not so cleanly as running first the sulphate liquor and then the tar acids from a bottom cock. The capacity of a "springing" tank may vary between 1,000 and 2,000 gallons, sometimes even greater, but a good average figure may be taken as 1,500 gallons.

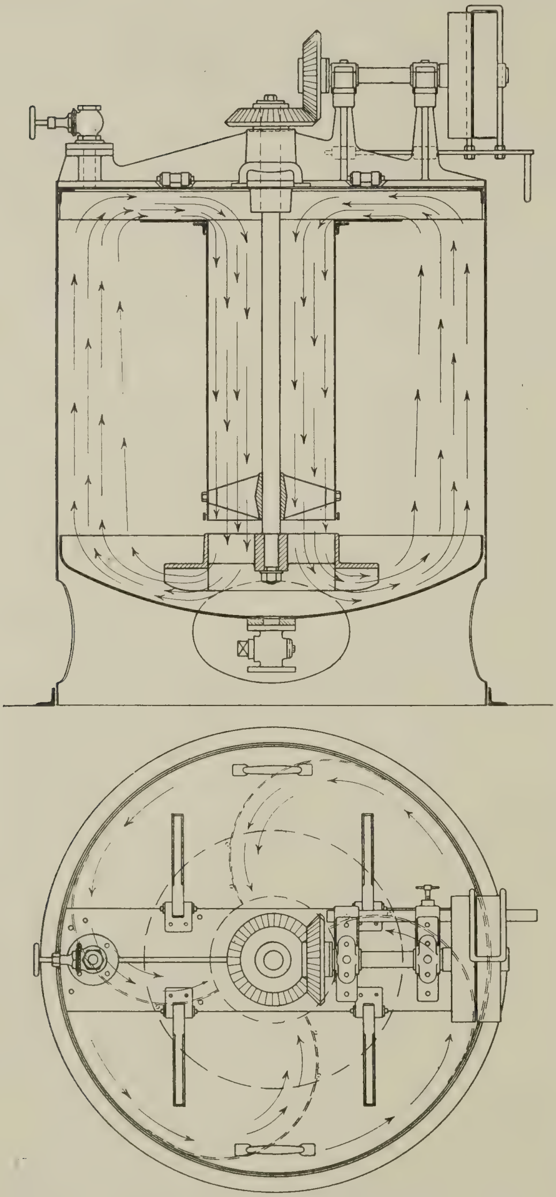


Fig. 76.—Washer by S. H. Johnson and Co., Ltd.

For working the CO_2 process more plant is required than that just described for the sulphuric acid process, and it is of a somewhat complicated nature. In addition to the washing tanks, the following are necessary: Two "carbolate" or "cresylate" boilers, a pump and suction sump, a reaction tower, two dividing tanks, a receiving tank for the tar acids, a receiver for the spent liquor (impure carbonate of soda solution), one finishing tank, one acid egg, one furnace for generating CO_2, a dust separating apparatus and tower for purifying and washing the CO_2, and the necessary pipe lines and arrangement for removing the water which sometimes separates from the gas. The gas may be drawn through the apparatus by the employment of a steam jet. According to the requirements of the Alkali Act, the spent gas must be purified before passing to the atmosphere. This can be done by passing it through one or other of tha well-known purifiers, and then allowing it to escape into the chimney stack, or it may be passed over the steam boiler fires, after travelling through a seal pot, as described when dealing with foul gas mains, pages 156, 157, Fig. 51.

Instead of employing a reaction tower, some distillers prefer to put in what are known as carbonating boilers. Of these the number required will vary according to the volume of "carbolate" to be dealt with, but it is advisable to erect four at least. No large divider boxes, receivers, or pump and sump are necessary if carbonating boilers are used. Of course, a pump for removing the spent liquor is required in both cases. The CO_2 is forced through the "carbolate" or "cresylate" via perforated coils, by means of a compression pump, and the acids which separate are either removed from the boilers by means of skimmer pipes, or the contents of the boilers are run into tanks with open tops, and after standing for a sufficient time the acids are removed by skimmer pipes. If desired the separation of the acids from the spent liquor may be carried out by running off from a bottom cock first the spent liquor and then the tar acids. When nearing the line of separation it is wise to run the liquid through a small dividing apparatus (p. 154, Fig. 49), thus avoiding any loss of acids.

Dealing with the CO_2 process, in which a reaction or carbonating tower is used, the pieces of plant named will be described in the order given above.

The "carbolate" or "cresylate" tanks are constructed of wrought-iron plates. Second-hand cylindrical boilers, if in good condition, make excellent tanks for this purpose. Whether new or second-hand tanks are used the joints must be well caulked, or leakage will take place. A hole is cut in the top to admit a 1½- or 2-inch inlet pipe ; two smaller holes are cut, one for the admission of a 1-inch steam-pipe, to which is connected a double-lap closed steam coil, and the other to allow the exit of the exhaust pipe of this coil. Both these holes should be at the top of the boiler-tank. The manhole and cover are allowed to remain : a manhole is sometimes useful for cleaning or inspection purposes. At one end of the boiler tank a 1½-inch hole is cut, the centre of which should be 3¾ inches from the bottom of the tank, and a 1½-inch pipe is fitted by means of a flange. This pipe is to conduct the phenolates to the pump sump. A cast-iron gland cock is fitted near the end of the pipe to regulate the flow into the sump, and it is wise to fit a further cock a few inches from the tank as a safeguard in case of accident. It is a good plan to arrange for a steam connection into this pipe in order to assist in removing any obstructions which may occur, and provision for the insertion of an open steam end into the tank is an advantage. At the opposite end of the boiler-tank a small mudhole 6 inches by 4 inches is cut. The lower edge of the hole must be as near the bottom

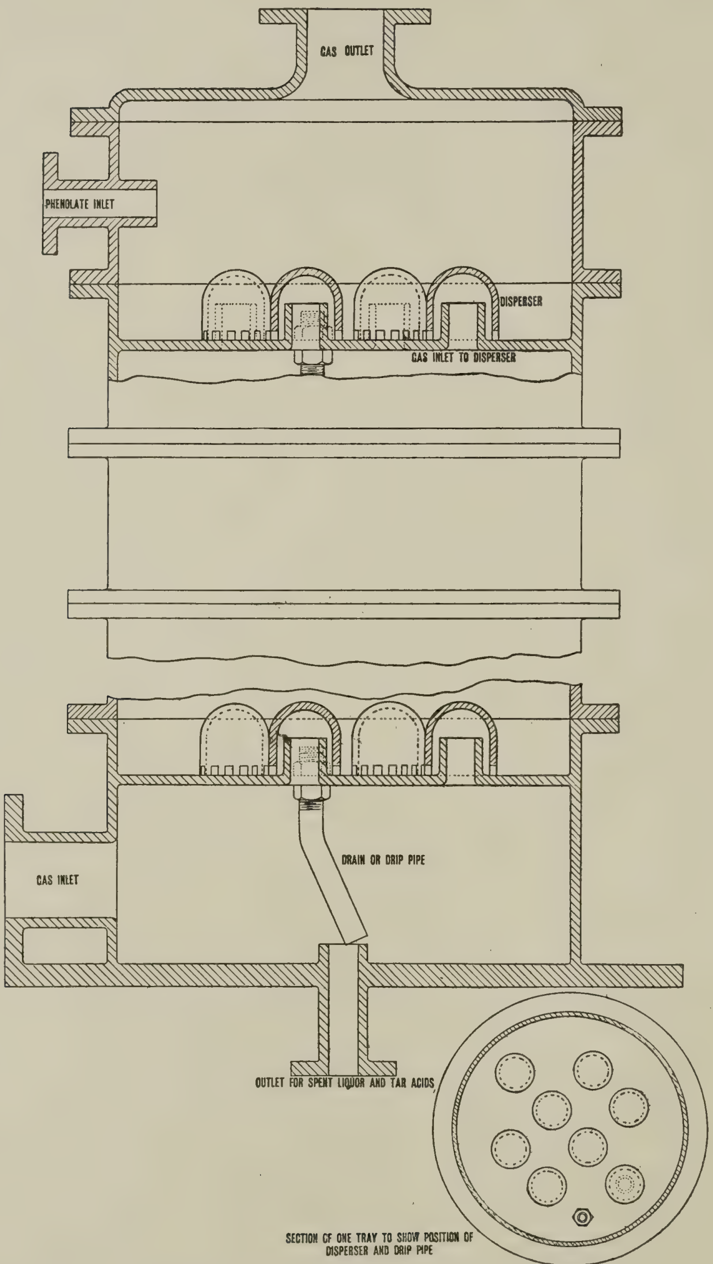

GAS OUTLET
PHENOLATE INLET
DISPERSER
GAS INLET TO DISPERSER
DRAIN OR DRIP PIPE
GAS INLET
OUTLET FOR SPENT LIQUOR AND TAR ACIDS
SECTION OF ONE TRAY TO SHOW POSITION OF DISPERSER AND DRIP PIPE

Fig. 77.—Carbonating or Reaction Tower (Plate Type).

as possible, and a casting is riveted on to carry the mud-hole cover. Both tank boilers may rest on 14-inch to 18-inch brick cradles, just a few inches above the ground level. The capacity of these tanks will vary, of course, according to the quantity of tar acids it is desired to make per day.

The pump may be of any good make, and the delivery vary between 1 inch and 1½ inches according to circumstances. It is erected a few inches from the ground level, in close proximity to the sump. A cast-iron vessel, about 2 feet deep and 1 foot in diameter, makes a suitable sump; a wrought-iron steam boiler dome will answer admirably. The sump is situated so that the top rises about 3 inches from the ground level, and if out of doors a wooden cover should be provided to keep out the rain. A few inches of puddle should be put in the hole before placing the sump into position.

There are two chief types of reaction or carbonating tower: the packed and the plate. The latter kind of tower is built up of cast-iron sections, while the former is constructed of wrought-iron plates. One of the best designs of plate tower is illustrated in Fig. 77. Naturally the size of the tower will vary according to the quantity of phenolate it is desired to decompose per diem. It may be approximately 15 feet high and 2 feet in diameter, the sections being 8½ inches deep over all. The number of dispersers in each section will vary according to its diameter. In a section of 2 feet diameter eight may be put in, the inlets to the dispersers being 1½ inches internal diameter and the diameter of the disperser hoods 4 inches. Each hood should have 12 by ½-inch openings in the circle. Only one internal drain-pipe of 1½-inch bore is necessary for each section. This pipe should be arranged to allow a seal of 1¾ inches of liquid on each plate. It is an advantage to provide an inlet for a steam-pipe so that the tower may be steamed out occasionally. The positions of the gas inlet and outlet, and also of the outlet for the spent liquor and tar acids, are shown in Fig. 77.

A packed reaction or carbonating tower is filled with foundry coke, earthenware balls, tiles, or one of the numerous patent tower packings. To pack a tower for this kind of work with coke is, in the author's opinion, a mistake; the coke soon becomes clogged and the available reaction surface is thereby much reduced. Often it clogs into hard masses, leaving fairly large holes here and there, called "rat holes," up which the gas travels, coming in contact with only the outside portions of moderately thick streams of liquid flowing in the opposite direction. Earthenware balls alone, or with small granite chips have given excellent results in the author's practice. In choosing a packing for a reaction tower of this kind, due regard should be given to the question of reaction surface; the greater this is the more rapid will be the decomposition. Three-inch earthenware balls with ½-inch hole give approximately 14·5 square feet of reaction surface per cubic foot of tower space; 2-inch balls with ½-inch hole, 23·3 square feet; and 1-inch balls with no hole, 37·3 square feet. Small granite chips, about 1 inch by ½ inch by ½ inch approximately, will give a very considerable reaction surface; about 100 square feet per cubic foot of tower space may be taken as a guide. A tower to deal with 2,500 gallons of phenolate solution, containing 20 per cent. of tar acids, per 24 hours, would require to be about 13 feet high and 4 feet in diameter, if packed with 1-inch balls with no hole, or if 2-inch balls with $\frac{1}{2}$-inch hole are used, the height of the tower may be 22 feet and the diameter 4 feet. If packed with 3-inch balls with $\frac{1}{2}$-inch hole, a height of 27 feet and a diameter of 4 feet 6 inches would be necessary; or if 4 feet of small granite chips and 18 feet of 3-inch balls were used as packing, then the height of the tower could be reduced to 25 feet, the diameter remaining the same. These figures are given as a guide, and may, of course, be varied according to requirements. The wrought-iron plates of which the tower is constructed need not be thicker than $\frac{3}{8}$ inch; $\frac{1}{4}$-inch plates are often used. If balls and granite chips are used together, two perforated plates are required, one as a false bottom and the other to rest on the top of the balls to support the granite chips. If balls are used alone, then one plate for the false bottom is all that is necessary. The plate for the false bottom should be $\frac{3}{4}$ inch to 1 inch thick with $\frac{1}{2}$-inch holes at 1-inch pitch, and supported on cross-bars about 1 foot 6 inches from the bottom of the tower, but the top plate need not be more than $\frac{1}{4}$ inch thick, the holes being of the same diameter and at the same pitch. Cast iron is the best metal to use. In the top or cover plate of the tower a 4-inch hole should be cut for the gas outlet pipe, a hole for a manhole of the usual size, and one for the phenolate delivery pipe, which latter leads to a spray arrangement. A 4-inch gas inlet is made with the centre at least 5 inches from the bottom of the tower, and to this a screwed flange is fitted. The end of the gas pipe is introduced through this flange so that 3 or 4 inches project on the inside. An inlet for a 1-inch steam-pipe to admit steam for steaming out the tower occasionally is made with its centre about 8 inches from the bottom of the tower, and in the bottom plate an outlet

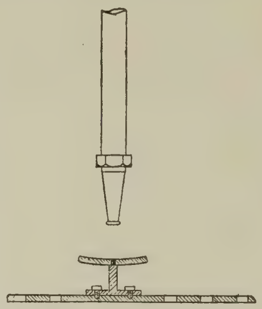


FIG. 78.—GURNEY'S JET ARRANGED FOR CARBONATING TOWER.

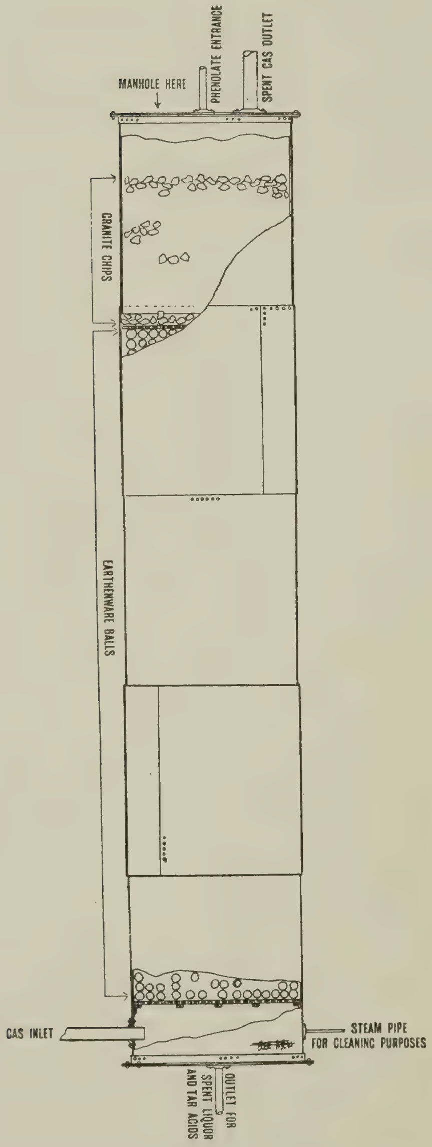


FIG. 79.—A CYLINDRICAL CARBONATING TOWER (PACKED TYPE).

about $1\frac{1}{2}$ inches in diameter is provided for the pipe which conducts the mixture of spent liquor and tar acids to the divider tank. The spray arrangement may be of the Gurney jet type (see Fig. 78), or built up of a 6-way piece connected to the delivery pipe inside the tower, and into which are screwed six lengths of $\frac{1}{2}$-inch wrought-iron pipe, about 22 inches long, and perforated with $\frac{1}{4}$-inch holes on the under side at a pitch of approximately 5 inches. These holes should be in alternate positions when one pipe is compared with the next. Details of the method of packing this type of tower, and the arrangement of the pipes, are shown in Fig. 79.

The divider tanks are made of wrought iron and much larger than those used in the tar-distilling plant. They are generally constructed square in plan, and the depth nearly twice that of the width. An average size is 2 feet 3 inches by 2 feet 3 inches by 4 feet deep, $\frac{1}{4}$-inch wrought-iron plate being used, the seams thoroughly caulked, and an angle rim placed outside. In order to promote the forward flow of separated spent liquor one divider tank is set about 9 inches higher than the other. The pipe to the tar acid receiver which is attached to the first or separating tank is of 1-inch wrought-iron pipe, and it is connected to a movable syphon pipe as shown in the diagram (Fig. 80). The lower tank is really a catch tank, which retains any tar acids escaping from the divider, and the pipe from the separating tank which leads the separated spent liquor to this tank and also the pipe which conducts the spent liquor from the catch tank to the spent liquor receiver are of $1\frac{1}{2}$ inches wrought iron. Any tar acid which separates in the catch tank, and it should be very little, is removed by skimming. Reference to Fig. 80 will give the method of fixing and other details.

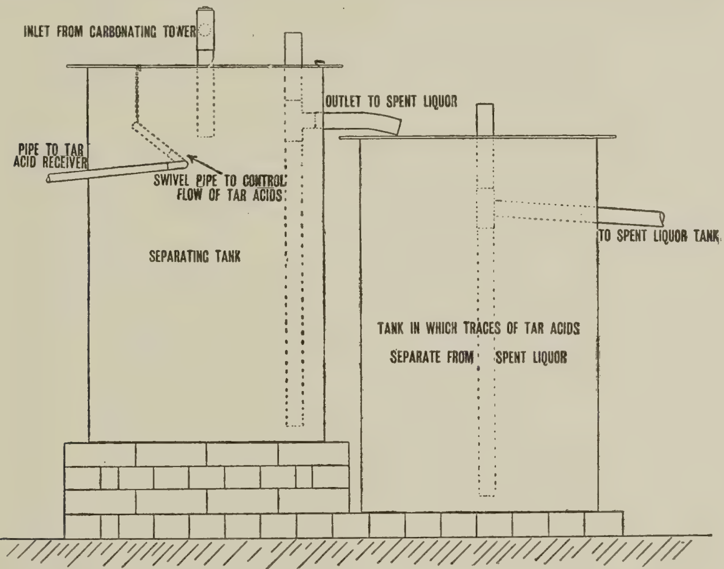

INLET FROM CARBONATING TOWER
OUTLET TO SPENT LIQUOR
PIPE TO TAR ACID RECEIVER
SWIVEL PIPE TO CONTROL FLOW OF TAR ACIDS
SEPARATING TANK
TO SPENT LIQUOR TANK
TANK IN WHICH TRACES OF TAR ACIDS SEPARATE FROM SPENT LIQUOR

FIG. 80.—DIVIDER TANKS, CO_2 TAR ACID RECOVERY PROCESS.

A wrought-iron riveted tank, square, rectangular, or cylindrical in shape, may be used for the tar acid receiver. It should be placed near the divider tanks, and, if in the open air, covered in, a lid being provided in the cover in order to make inspections. The outlet pipe, which is of 1-inch wrought-iron, is with advantage connected with a movable skimmer pipe, as generally on standing some spent liquor separates from the tar acids and settles to the bottom. In order to facilitate this separation, and thus save some sulphuric acid, a closed steam coil may be placed at the bottom of the tank and fed with exhaust steam. The tar acids should be kept at a temperature not exceeding 75° F. As regards the size of the tank, this will vary according to the volume of tar acids it is desired to deal with per day. The tank may be erected on the ground level, or raised several inches, according to circumstances.

The receiver for spent liquor should be of wrought iron, and a good-quality second-hand steam boiler answers admirably. It should be placed partly or wholly below the ground level, according to circumstances. The hole must be lined with well-made puddle before putting the tank in. A manhole with tight cover, a dipping pipe which also makes an air vent, and holes for inlet pipe and suction pipe are required. The dipping pipe should reach about 9 to 12 inches above the ground level, and need be only $\frac{3}{4}$-inch internal diameter, the inlet pipe hole $1\frac{1}{2}$ inches, and the suction pipe 2 inches. If the tank is only partly below ground, the dipping pipe is not necessary; a $\frac{3}{4}$-inch hole will suffice.

A lead-lined tank must be put in for the purpose of carrying out the finishing operation. The tank may be rectangular or square in plan, and built of well-creosoted timber, lined on the inside with stout "chemical" lead. Five or seven pound lead is quite thick enough. There is no need to provide for any openings in this tank, as the finished acids can be most conveniently removed to the acid egg by means of an ever-ready syphon (Fig. 81). The tank should be placed as near to the acid receivers as possible, and on the ground level.

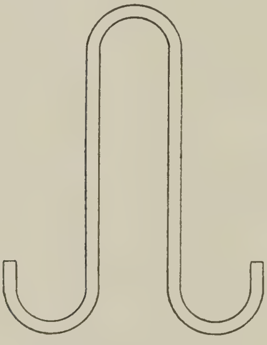


Fig. 81.—Ever-ready Syphon.

The acid egg may be constructed of cast iron, wrought iron, or lead. Of the three metals, lead is the least likely to suffer from corrosion, but to construct a large egg, say, of a capacity of 150–200 gallons, is an expensive matter. Cast iron is liable to fracture, and in the author's opinion a wrought-iron egg will give excellent results and suffer very little corrosion if properly managed. There is no difficulty in making a wrought-iron egg of large size, and it is cheap. If the ends are well dished, there is no need to put in a central stay, which is of course necessary if the egg is made with flat ends. The egg should be provided with a pressure gauge, a safety-valve, a 6-inch circular hole with strengthening ring and draw-up manlid, a 1-inch air inlet, the pipe just entering, a $1\frac{1}{2}$-inch or 2-inch outlet pipe, which should reach to within $1\frac{1}{2}$ inches from the bottom of the egg, and a 1-inch drain cock. For the position of the various fittings, reference to Fig. 82 should be made. The egg is placed below ground, immediately under the finishing tank, and a brick-lined sump made under the drain cock as shown in Fig. 82. When setting the egg, a fall of 4 inches in 10 feet towards the drain cock must be allowed. As already mentioned, the tar acids are transferred from the finishing tank to the acid egg by an ever-ready syphon; this piece of apparatus is illustrated in Fig. 81.

The tar acids may be stored in wrought-iron tanks of any convenient shape and size: they should be covered in and a manhole and lid provided. A 1½-inch drain cock of cast iron is fitted on the bottom of the tank, and the cock to be used for emptying purposes must be fitted on the side with its centre line 4 inches from the bottom of the tank. It should be a 2-inch cast-iron gland cock. Storage tanks may be supported on brick or concrete piers, at a convenient height for filling barrels. Arrangements should be made for connecting the emptying cock with mains for filling railway tanks or tank boats, also for connecting up to a steam supply in order that an open steam end may be inserted into the tank to steam it out when it requires cleaning.

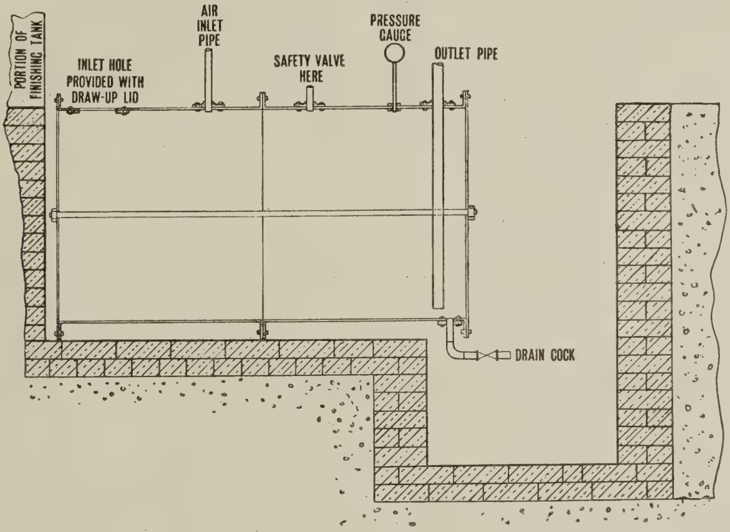


Fig. 82.—Egg for use on Carbolic Plant, Etc.

In the CO_2 process, one of the most important pieces of apparatus is that from which the supply of carbonic acid gas is drawn. Sometimes the waste gases from the flues of a steam boiler, under which coke is burned, are used, after purifying, for this purpose. This method cannot be recommended. The same may be said of the method of using waste gases from an ammonia-distilling apparatus. Undoubtedly the best plan is to employ a special generator, built just the right size to supply the plant with sufficient purified gas when it is working under full pressure.

There are several patent CO_2 generators put on the market by various makers, but it may be preferred to build one's own generator. Three chief designs of generator exist: The flat or dead hearth; the firegrate, in which the coke is burned on firebars; and the water-bosh or water-sealed generator. In the first type of generator the fuel is fed to the fire at the top, and in burning it rests on the firebrick bottom of the generator. A cast-iron door about 18 inches by 10 inches is put in on a level with the bottom, on the front of which is an air grid to regulate the admission of air, and through which the clinker is withdrawn. The gas is taken off from the top of the generator. With this type of generator, trouble often arises with the air regulation, the fire burns very unevenly, and during the cleaning or clinkering process much unburned coke is withdrawn with the clinker, and the uniformity of the gas is upset for an inordinate length of time. The clinker is often considerable. In the second type of generator the air regulation is under better control, especially if the ashpit is closed by a door on the face of which air grids are fitted. The fire burns much more evenly, but unless the bars are water-cooled they are rapidly burned away; even when they are cooled with water, a good deal of trouble is experienced

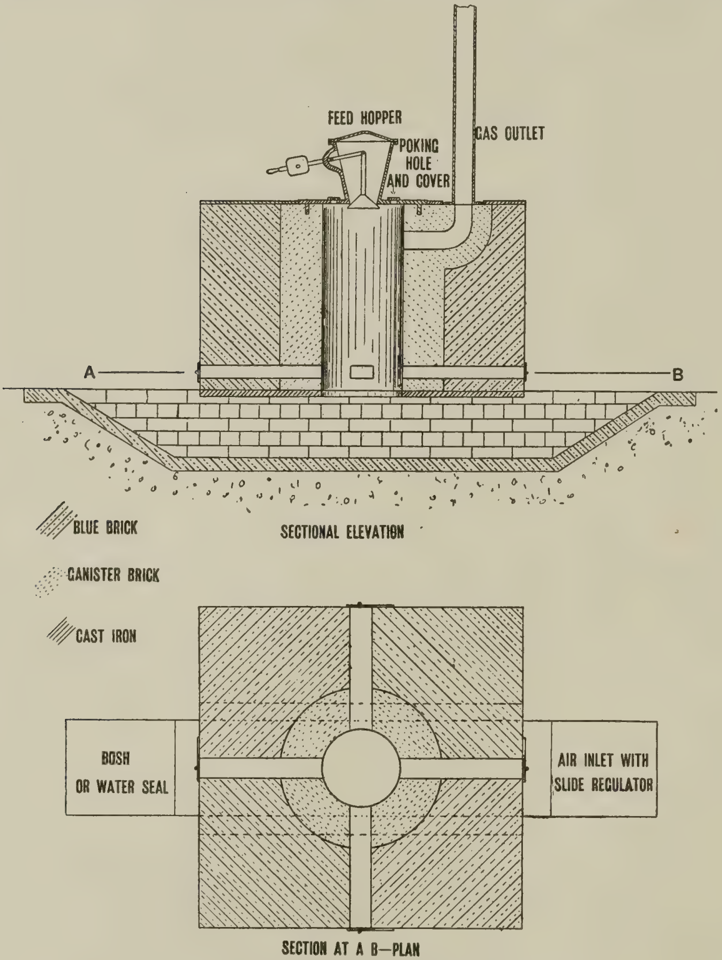


Fig. 83.—Furnace for Generation of CO_2.

in this direction, and during the removal of the clinker much excess of cold air is admitted to the generator.

The last type of generator is, in the author's opinion, the best. Three generators which he designed, and which varied somewhat in detail, both yielded excellent results. They gave very little trouble as regards clinker, and no trouble due to excessive air admission and its resulting uneven quality of gas during cleaning. The fuel is fed in from the top via a hopper and bell valve, and the poking down carried out

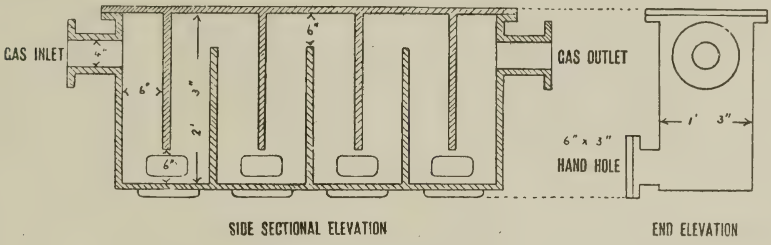


FIG. 84.—DUST SEPARATOR.

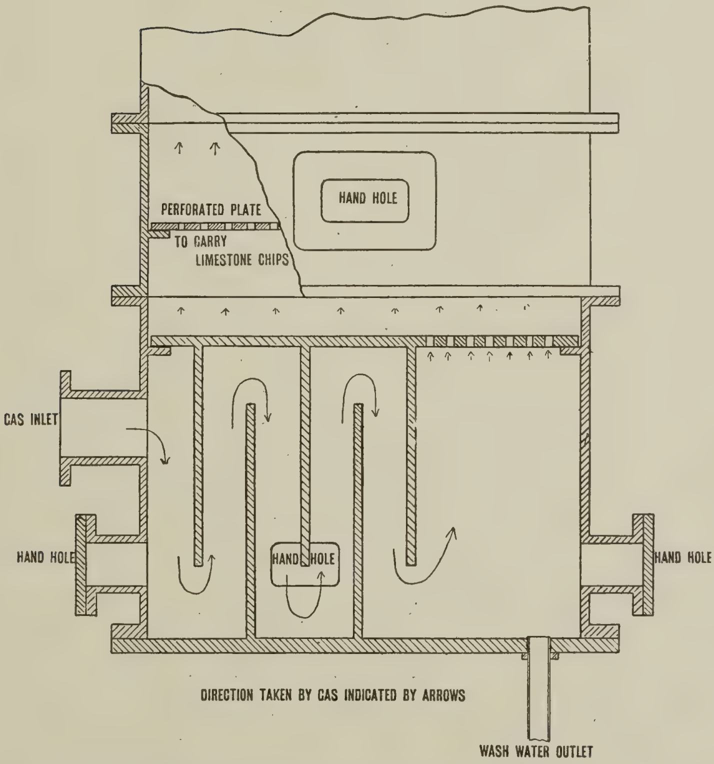


FIG. 85.—PURIFYING TOWER WITH DUST SEPARATOR BUILT IN BOTTOM.

through poking holes. Ashes, with very little clinker, are removed through the water-seal or bosh. The gas is drawn off through a firebrick-lined flue in the side of the generator near the top. This flue bends round in such a fashion that the position of the exit is at the generator top, and there it is connected with a cast-iron gas pipe. Air inlets are provided at each of the four sides of the generator, and they are made so that the quantity of air can be regulated by slides running in frames built in the brickwork. The generator is lined with best ganister brick; when working properly, the temperature of the generator is so great as to fuse most, if not all, qualities of firebrick. A staging, supported on brackets, is fitted round the top; this is for the man to work upon. The generator top is also covered with a cast-iron plate. It is advisable to strengthen the structure with light backstaves and tie-rods. Fig. 83 will show the shape and many details associated with this type of generator.

As the gas leaves the generator it carries with it a fair amount of dust, and also impurities such as sulphur dioxide and sulphuretted hydrogen, together with some moisture. These it is necessary to separate as far as possible before the gas enters the reaction tower, or if carbonators are used, these vessels. The dust must be separated first, and then the gaseous impurities, and finally as much of the moisture as possible. A dust separator may be built in the bottom portion of the washing and purifying tower, or erected as a separate piece of apparatus. It should be of cast iron. A simple and yet efficacious piece of apparatus for carrying out the dust-separating operation is shown with approximate measurements in Fig. 84, and Fig. 85 shows one built in the bottom of a purifying tower. If the dust separator is erected as a separate piece of apparatus, it must be placed between the generator and purifying tower. In the event of a water-sealed CO_2 generator being used, it is a good plan to place the dust separator as near the generator as possible. The object of this is to keep the separator hot in order to avoid the condensation of moisture, which, if it takes place, will convert the dust into mud. It is necessary to remove frequently the dust from the separator in order to prevent choking.

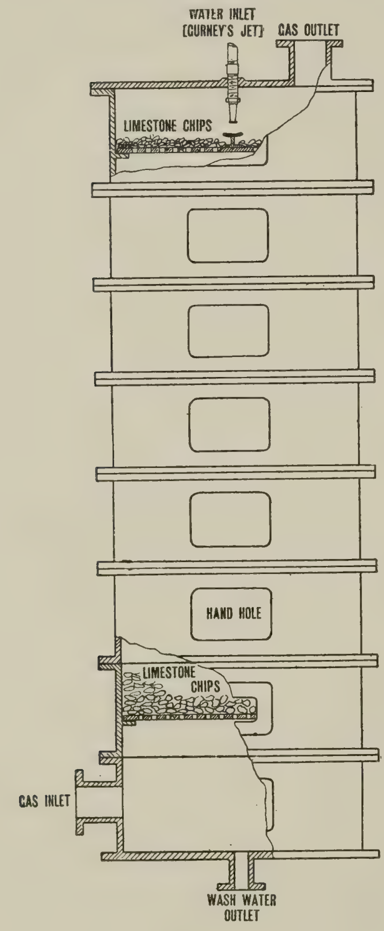


Fig. 86.—Diagram illustrating a Type of Purifying Tower without Dust Separator.

The purifying or washing tower (Fig. 86) is best constructed of cast-iron sections, square or round in plan. If round, each section should be about 3 feet in diameter, and if square, about 2 feet 6 inches by 2 feet 6 inches. In either case each section should be 12 inches deep. Each section carries a grid, supported on a ridge cast on the section (see Fig. 86). The grids may be of wood or mild steel; the writer is inclined towards the use of mild steel, as in his experience the amount of corrosion is exceedingly small. Wooden grids eventually become soft and rotten. Mild steel grids are best made of $\frac{1}{2}$-inch plate drilled with $\frac{7}{16}$-inch holes at 1-inch pitch. Each grid should be covered with a layer of limestone chips about $1\frac{1}{2}$-inch size, to a depth between 5 and 6 inches. A hand hole is made in each section, the lower portion of which must be on a level with the top of the grid or tray. The number of sections in the tower will vary according to the quantity of gas passing through it per day. For a plant burning 800 lbs. of coke per 24 hours, a tower of eight sections 2 feet 6 inches square will prove quite suitable.

The bottom section has no grid, but should have a hand hole, and into this section the gas enters by a 4-inch cast-iron pipe, the centre line of which is 6 inches from the bottom of the section. A 1-inch or $1\frac{1}{2}$-inch exit for wash water is provided for in the bottom of the section. To the top section is fitted a 4-inch cast-iron gas outlet pipe, and also a 1-inch water inlet. The water is distributed over the top grid by means of a Gurney's jet (Fig. 78). In order that the gas pipes conducting the purified gas from the washing tower can be cleared of any obstruction which may occur—and obstructions have occurred occasionally in the author's experience—they are fitted with fourway pieces arranged as shown in Fig. 87, the removal of the blank flanges making it easy to shift the obstruction.

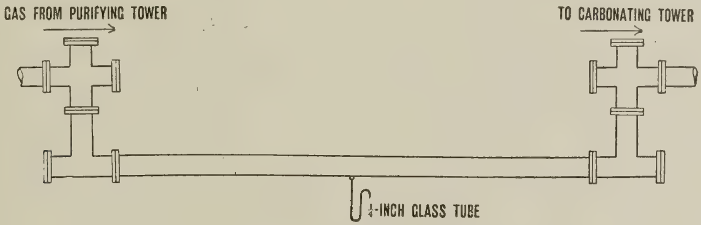


FIG. 87.—U-BEND TO SEPARATE WATER FROM GAS.

To remove the water which condenses out of the gas (especially in cold weather) and settles in the lowest portion of the gas main, the following simple plan devised by the author may be used. The gas pipe is allowed a gentle fall until it reaches to within about 14 feet from the point of entry into the carbonating tower, or first carbonating boiler. A flat U-bend is made in the pipe, and in the lower end of this, about the middle, and underneath the pipe, a $\frac{3}{4}$-inch hole is drilled. Into this hole is inserted a cork, into which is fitted a piece of $\frac{1}{4}$-inch bore glass tube, bent, as shown in Fig. 87. The depth of the U is made so that it just allows the water in it to resist the pull on the plant without being drawn out of the tube. Immediately any water collects in the gas pipe, it is automatically removed by the glass U-tube without the seal being broken and the admission of air.

A plant of improved design for the recovery of crude carbolic acid or crude cresylic acid from tar oils by the CO_2 process, designed by Blair, Campbell, and McLean, is illustrated in Figs. 88, 89, 90. Briefly, the working of this plant is as follows :—

The distillates containing tar acids are washed with caustic soda of approximately 23° Tw., or recausticised spent liquor, in special mixers, which are designed so as to ensure a thorough and complete contact between the two materials without producing undesirable emulsions. After a thorough agitation the contents of

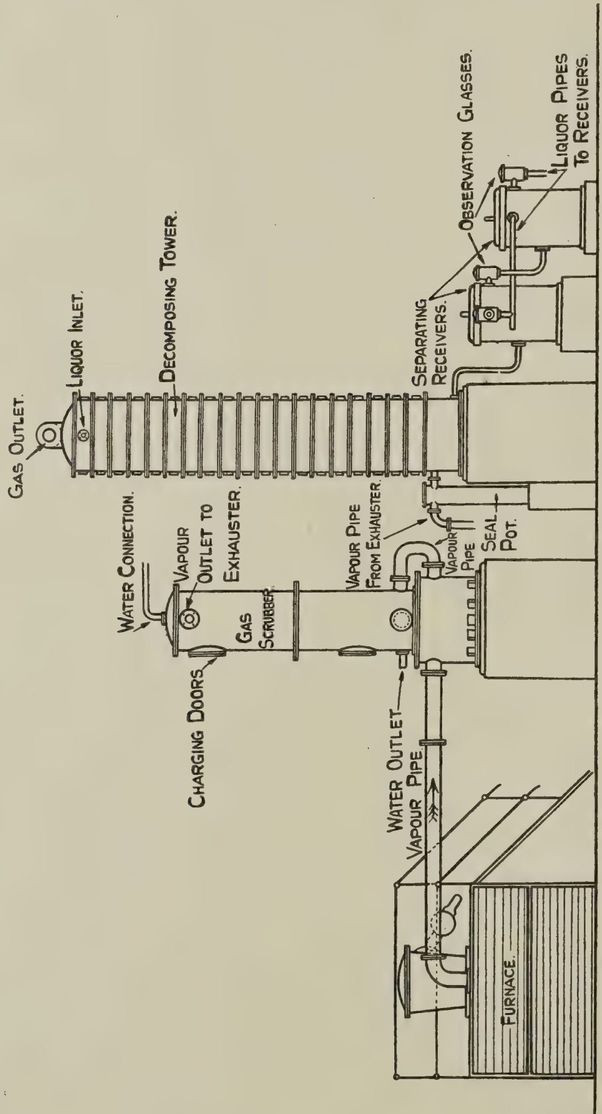
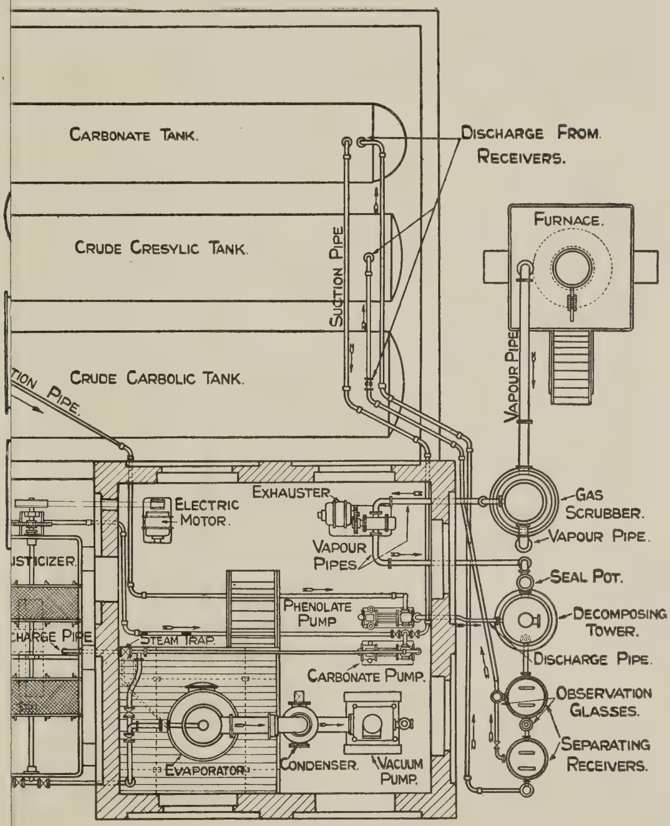


Fig. 89.—Blair's Crude Carbolic Plant.



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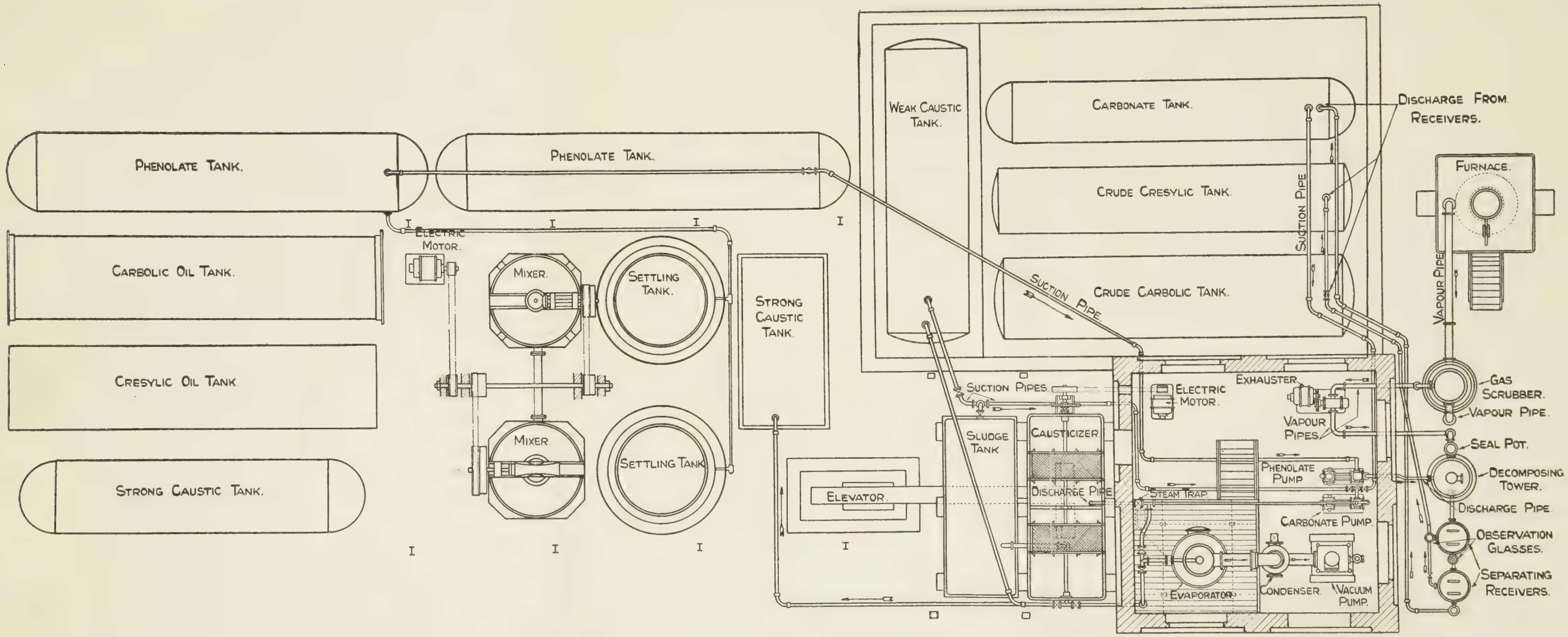

Fig. 88.—Blair's Crude Carbolic Plant; Lay-out Arrangement.

To face page 216.

the washers or mixers are transferred to settling tanks, in which the phenolate and oil separate, the oil, of course, rising to the top. When separation is complete, say, in an hour or two, the oil and phenolate are transferred to suitable tanks to await further treatment.

The phenolate solution, or carbolate, is passed into an improved type of decom-

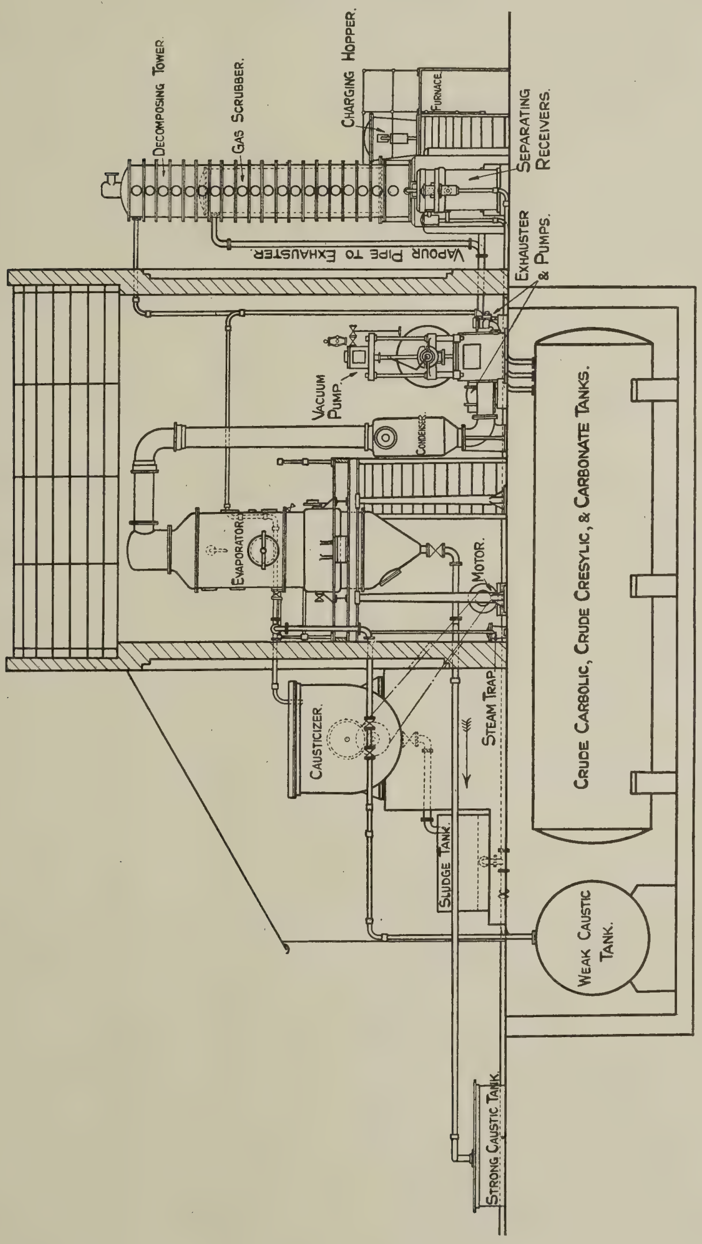

FIG. 90.—BLAIR'S CRUDE CARBOLIC PLANT.

posing or reaction tower, of the plate type fitted with bells, and very similar in principle to a benzole still fractionating column, where it meets with carbon dioxide under pressure, the counter-current system being adopted. The carbon dioxide is prepared in a furnace or generator of the water-bottom type, and before entering the reaction tower is cleaned from dust and washed free of sulphur dioxide and sulphuretted hydrogen in the scrubbing tower shown in the figure.

The spent liquor or impure carbonate of soda solution, as it leaves the decomposing tower, is run to a storage tank, in which it is allowed to settle for a while in order to remove the small quantity of tar acids which occasionally separates on standing, and after that period the clear liquor is passed into a Blair vacuum evaporator and concentrated to the requisite strength for recausticising. On leaving the evaporator it is charged into the causticiser, in which it is causticised with lime in the usual way, then filtered and run to the strong caustic tank to remain in readiness for further duty in the process.

As the tar acids leave the decomposing tower they pass through separating receivers into storage tanks to await further treatment, or in the case of crude carbolic acid to be dealt with as described under the refining of this material (see pages 241–243).

The CO_2 process is dealt with in general from a manufacturing point of view in Chapter XI.

In the CO_2 process the spent liquor, which is really an impure solution of carbonate of soda, is converted into caustic soda by causticising with lime. The pieces of plant required for carrying out this process are: Two or three causticisers, two caustic soda tanks, a filter, a pump, and an evaporator. These pieces of plant will be described in the order given.

The causticising tanks are cylindrical and built of wrought-iron or mild steel plates. They may be horizontal or vertical; the latter is the best type to use. Each tank is fitted with a mechanical agitator, an open and closed steam coil, a skimmer pipe, a grid or basket made of bar iron, at the top if of the vertical type, and a gate or treacle valve having a 6-inch opening on the bottom. They should be erected above ground, best on rolled steel joists and stanchions, and above the filter. A water supply should be arranged for over each causticiser.

It is advisable to put in two caustic soda tanks, one for strong caustic soda from the causticisers and the other for weak caustic soda or " weaks "—the washings of the lime mud from the causticisers and the filter. These tanks may be square or rectangular in shape, according to circumstances, and constructed of mild steel plates, the seams being thoroughly caulked. A suction pipe which can be raised and lowered should be fitted to each tank. They should be erected on the floor level, as close to the causticisers as possible.

The filter is situated immediately under the causticisers, and should be of such a size that it will hold the lime mud from all the causticisers at the same time. It is constructed of mild steel plates, $\frac{3}{8}$ inch to $\frac{7}{16}$ inch in thickness, and it is best built rectangular in plan. The seams should be double riveted and thoroughly well caulked, and on one side as near the bottom as possible a 2-inch suction pipe is fitted. Two sets of perforated plates are required: one to form the base of the filter bed and the other to cover the top. These plates are of mild steel, $\frac{1}{4}$ inch thick, and drilled with $\frac{1}{2}$-inch holes at a pitch of 2 inches. The bottom set of plates are laid on Staffordshire blue bricks at a height of 6 inches, arranged in rows 18 inches apart, on the bottom of the filter. An excellent filter bed is made by using graded granite chips, and a top layer of coke breeze, upon which the other set of perforated plates are placed. The thickness of each layer of granite chips and the approximate sizes are as follows: On the bed plates a layer of $1\frac{1}{2}$-inch to 2-inch chips 4 inches deep is placed; then a 3-inch layer of $1\frac{1}{2}$-inch to 1-inch chips; then a 3-inch layer of $\frac{1}{2}$-inch to $\frac{3}{4}$-inch, and then a 3-inch layer of $\frac{1}{4}$-inch and $\frac{1}{8}$-inch chips, above which a 2-inch layer of coke breeze is placed. To dry the lime mud further than is possible with a filter, and to recover the maximum amount of caustic soda in the form of "weaks," the employment of a centrifugal machine is necessary.

Any good pump of the ram type may be connected up to the outlet at the bottom of the filter. The pump should have a 2-inch suction, and the glands on the water end should be packed carefully with "ammonia" packing. This packing is the least attacked by the weak caustic liquor. The pump not only assists in the filtering operation, but pumps the weak caustic liquors, washings, and filtrate into the evaporator. A connection with the "weaks" tank to the pump suction is made through a by-pass.

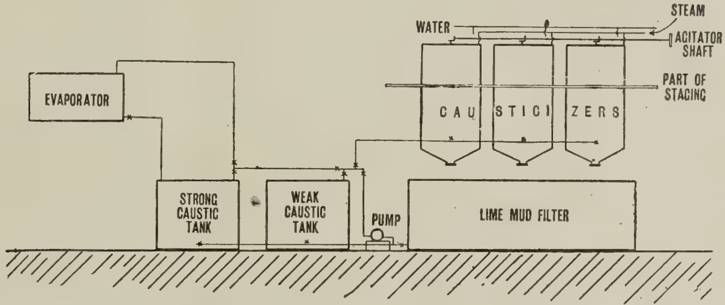

FIG. 91.—DIAGRAM SHOWING ONE METHOD OF ARRANGING CAUSTICISING PLANT.

If considerable quantities of weak caustic liquor have to be concentrated, then it is advisable to put in a vacuum evaporator and its appurtenances, using exhaust steam as the heating medium. However, this is seldom necessary in a tar distillery. The usual method is to cover the bottom of a tank of suitable size with a series of coils of 2-inch or 3-inch steam-pipe. A reliable type of steam trap should be fitted on the exhaust end of the coils. To get the best results, the "weaks" must be allowed to stand as long as possible, in order to deposit any lime mud suspended in it, as this mud will, if it gets into the evaporator, coat the coils and thus hinder the rate of evaporation. In any case it is as well to clean occasionally the steam coils by scraping them, and then washing down. The evaporator is erected on rolled steel joists and stanchions for preference, and at a height above the ground level which will permit of the concentrated caustic liquor running into the storage tank by force of gravity. Fig. 91 illustrates diagrammatically one method of arranging a causticising plant.

If it is desired to manufacture 95–97 per cent. cresylic acid, then it is necessary to submit the crude, as it comes from the carbonating tower, to a process of distillation and air blowing. The pieces of plant required to carry out the manufacture of this kind of cresylic acid are as follows : A still charging tank, a mild steel still with a fractionating column, a condenser coil and tank, collecting box, water separator, bottoms receiver, pitch bay, cresylic and carbolic receivers, acid egg and blowing boiler, and foul gas mains.

It is very convenient to erect the undistilled crude cresylic storage tank at a higher level than the still top and in close proximity thereto. By doing so the still can be charged by force of gravity, and only one passage through the acid egg is necessary ; two would be required if the storage tank is placed at a low level. The tank may be of any convenient shape, constructed of mild steel plate, covered in and provided with manhole and lid. An inlet pipe and dipping hole are put into the top, and the outlet pipe for charging the still is placed on the side, its centre line being 4 inches from the bottom. A very convenient diameter for the charge and inlet pipe is 2 inches. It is advisable to put a 1-inch drain cock in the bottom of the tank, through which any sodium sulphate liquor which separates may be drained away. The separation of the liquor may be expedited by keeping the acid at a temperature of about 70° F. by means of a small steam coil. Every endeavour should be made to keep this liquor out of the still.

A cresylic still is constructed of mild steel plates throughout, and of a similar shape to a tar still. The fittings, such as manhole and lid, charge inlet, swan neck, safety-valve, tail pipe, etc., are also similar to tar still fittings, and the same may be said of the settings, fireplace, flues, etc. The reader is therefore referred to the details given under tar stills in Chapters VI and VII.

As a certain amount of carbolic acid is present in the crude cresylic, and the value of the former is generally greater than that of the latter, it is advisable to separate these by means of a fractionating column. This piece of apparatus is made of cast iron and built up of sections of approximately 2 feet in diameter and 9 inches in depth. The size varies somewhat according to the type of column, and the height of it, to a large extent, according to the degree of perfection to which it is desired to conduct the fractionations. A good average number of sections used in a column is fifteen ; this includes the top and bottom sections. One of the best types of fractionating column is described and illustrated on pages 252 and 258. The tower is supported on steel stanchions and joists on a convenient portion of the brickwork at the still top. A return pipe is fitted into the underneath portion of the bottom section of the tower and inserted into the still top, a U-bend being made in the pipe to act as a seal. The bottom section is also connected to the swan neck of the still, and an arrangement is made for by-passing the tower, so that during the water and cresylic acid stages the vapours can be conducted direct to the condensing worm. These various details are illustrated diagrammatically in Fig. 92. It is a good plan to arrange that all the sections can be drained after each operation.

The condenser coil and tank are similar to those used with tar stills (see page 150) and so is the collecting box (see page 154). For the separation of the water and tar acids as they run into the collecting box, this piece of apparatus is connected to a separator of the same kind as that described on page 154, but it is arranged for the water to be removed from the top of the separator and the tar acids from the bottom.

After a certain portion of the contents of the still have been worked off, the residue is allowed to cool a little and then run into a tank, known as a "bottoms" receiver, to be worked up with the "bottoms" from other operations when a sufficient quantity has accumulated. A horizontal boiler tank makes an excellent receiver. It is set below the still run off or tail pipe, and is connected up to the still by this arrangement. Connection is also made with a pump, or it is arranged that the receiver can be tightly closed and then emptied by air pressure. In this case it is connected to an air compressor, and an outlet tube is fitted so that it reaches to within about 2 inches from the bottom. As the "bottoms" become viscous on cooling, it is advisable to put in a closed steam coil of one lap, built of 1-inch wrought-iron pipe, in order to warm them up prior to charging them into the still. The receiver should have a manhole and lid of the usual size.

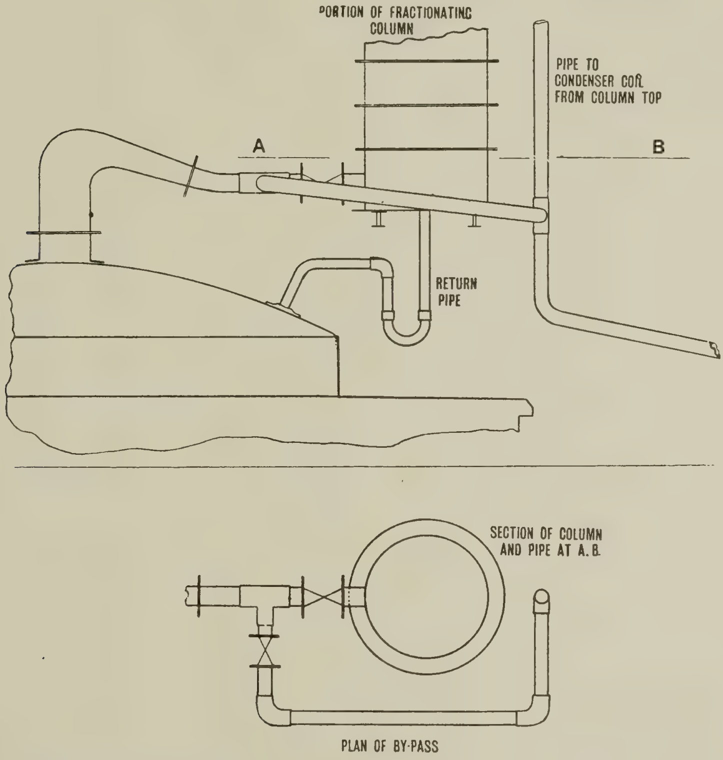
PORTION OF FRACTIONATING COLUMN
PIPE TO CONDENSER COIL FROM COLUMN TOP
A
B
RETURN PIPE
SECTION OF COLUMN AND PIPE AT A.B.
PLAN OF BY-PASS

Fig. 92.—Diagram illustrating a Method of attaching Fractionating Column to a Cresylic Still and arranging a By-pass.

The " bottoms " are finally worked to pitch, and the pitch is either run off and mixed with a big batch of pitch from the tar stills, or else run into a special bay. If a special bay is desired, it is constructed in a similar manner to the large bays described on page 161, but is, of course, much smaller. A 4-inch pipe is connected to the tail pipe of the still for running off the pitch, and by means of a reducing T-piece, and the necessary cocks, the " bottoms " pipe, which is 2 inches in diameter, is connected to the pitch pipe.

Receivers for the cresylic and carbolic acid may be constructed of mild steel, and square, rectangular, or cylindrical in shape. If cylindrical, they may be horizontal or vertical, and it is a good plan to arrange so that the contents can be transferred by air pressure to storage or mixing tanks, in the case of carbolic acid, and to an air-blowing boiler for purification in the case of cresylic acid. Square or rectangular tanks are not suitable, if it is desired to remove their contents by air pressure; if they are put in they will have to be connected up to a pump or egg.

Cresylic acid from the still generally contains sulphuretted hydrogen and other sulphur compounds in sufficient quantity to render it foul in smell. It is necessary to sweeten the acid before despatching to customers, and this process is carried out in a large cylindrical boiler tank, placed in a horizontal position. Along the bottom of this tank is fitted a perforated coil of 1-inch wrought-iron tubing, through which air is passed during the operation. The top of the tank is connected to a 2-inch foul gas main, which, in its turn, is connected with a purifier or a seal pot and ejector. In the latter case the gas is burned underneath the steam boilers, and the ejector may be employed to draw air through the cresylic acid in the tank by leaving an open end on the upright length of the coil, just a little above the point at which it enters the boiler. The foul gas may, of course, be drawn through the purifier by an ejector and the same method of air-blowing the cresylic acid employed. If an ejector is not used, it is necessary to connect the perforated air coil to an air compressor. It is as well to provide this tank with a manhole and lid of the usual dimensions. An inlet pipe is also required, and an outlet pipe, to which is fitted a cast-iron cock through which barrels are filled. A by-pass should be connected to the outlet, so that when it is desired to load the acid into a railway tank wagon it can be run into an egg, and then filled into the wagon by means of air pressure. A suitable kind of egg has already been described on page 210.

In connection with the recovery of tar acids, the Peppers' patent extractor, which is manufactured by W. C. Holmes and Co., Ltd., is worthy of notice, and a diagrammatic illustration of this plant is given in Fig. 93.

For the satisfactory manipulation of Peppers' patent extractor two tanks are required to hold caustic soda lye of different strengths and one tank to hold unwashed oil. There are two mixing chambers and separation tanks, one for the extraction of crude carbolic acid and the other for crude cresylic acid. Before the extraction process is commenced the oil and caustic soda lye are heated to a suitable temperature, approximately 80° F., by means of a dry steam coil in the bottom of each tank. The strength of the caustic soda lyes will depend upon whether the tar acids are to be recovered by the CO_2 process or by the sulphuric acid method. In the case of the former they may be approximately 1·115 specific gravity for carbolic acid and 1·125 for cresylic acid, and of the latter 1·125 for carbolic acid and 1·225 for cresylic acid.

Unwashed oil from the storage tank and caustic soda lye of the determined strength for the extraction of crude carbolic acid are run into the conical-shaped device at the mouth of the mixing chamber A, which, as will be seen on inspecting the diagram, Fig. 93, is fitted with a series of sectional plates. The flow of oil and lye is controlled by the cocks B and C.

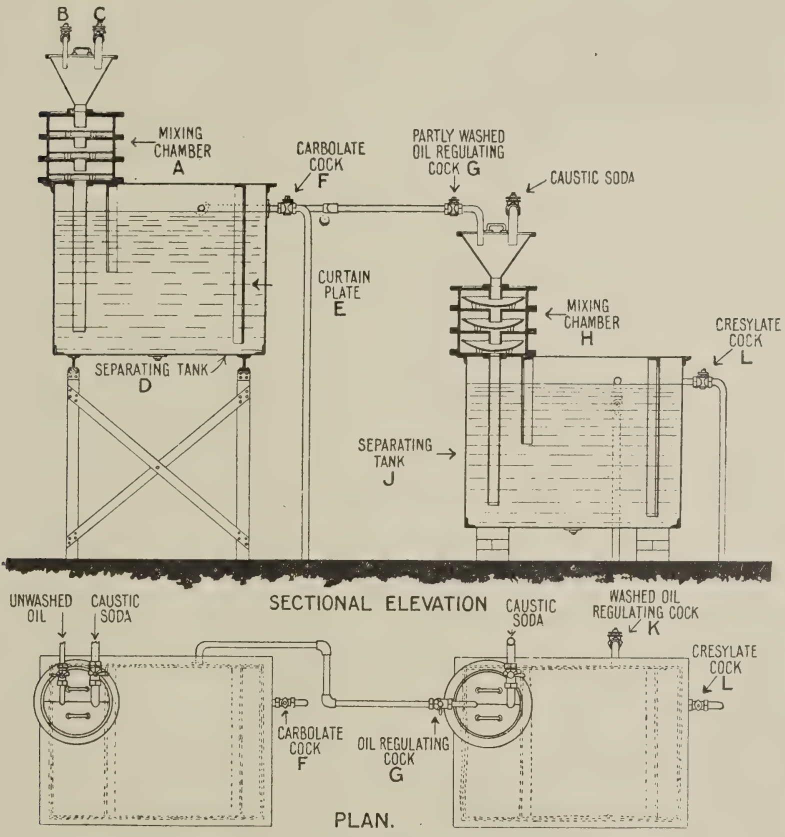

Fig. 93.—Peppers' Patent Continuous Extractor for the Recovery of Carbolic and Cresylic Acids.

On leaving the conical mouthpiece the two liquids enter into section 1, which consists of a plate with slotted holes at the side, and they splash on this plate and run through the slots into section 2, which consists of a plate with a centrally fixed hole to lead the oil and soda into section 3, which is similar to section 1. This process of agitation continues until the mixture of oil and soda has passed through the whole six sections. On leaving the mixing chamber A the two liquids enter the small tank D, in which separation takes place.

The separated carbolate passes through a small space at the bottom of the curtain plate E, and then through the cock F, on its way to the carbolate stock tank, to await further treatment.

The partly washed oil flows through the regulating cock G, and is led into the second mixing chamber H, along with caustic soda lye from the storage tank containing that of the correct strength for the recovery of crude cresylic acid.

The second mixing chamber is of slightly different construction to the first, but is practically on the same principle. It consists of a conical-shaped mouth, like the one in the first chamber, and flat plates with centrally fixed holes to which are fitted small neck pipes on the bottom sides, also three shallow dished pans with slotted openings round the edge. These dished pans are placed between the plates.

The liquids on entering section 1 pass through the central hole into the dished pan beneath it, flowing through the opening at the edge on to section 2, where they splash together and run through the central hole into the dished pan, as in section 1. This goes on through all the sections. On leaving the last section the mixture enters the tank J, which is similar in construction to tank D on the crude carbolic acid portion of the plant. The separation of the oil and cresylate takes place in this tank, the oil flowing through the regulation cock K, and the cresylate under the curtain plate and through the cock L, into their respective storage tanks.

APPENDIX

Within a recent date a new piece of plant has been put upon the market by the use of which tar acids may be extracted from those tar oils which contain them, creosote emulsified with water, and coal tar pitch with coal tar oil. This piece of plant is known as the " Premier " Mill, and a reference to Fig. 94 will show that it consists of an outer casing which surrounds a rotor " R." This portion of the mill is a perfectly smooth steel cone which is made to extremely fine limits as regards accuracy. It is fixed to the spindle " SP " which is mounted in special bearings, and it works in close relation to a fixed surface " CS " which forms part of the casing, the arrangement being very similar to the action of the clutch on a motor-car. The working surface of the rotor " RS " is arranged so that there is a very fine clearance between it and the surface of the casing " CS." In this arrangement a metal surface rotates in very close proximity to a fixed surface at a speed which may be varied between 1,000 and 5,000 r.p.m. The rotor should on no account be adjusted so that it actually touches the casing " CS," but it can be so regulated that the actual clearance will be anything from three-thousandths of an inch to two- or three-hundredths, according to the nature of the work to be done. It is very necessary to remember that when the machine is being used with hot material expansion takes place. On this account a fine clearance should not be set until the machine has become heated up to the temperature of the material which is to pass through it. A good rule to remember is: Never use a finer clearance than the job requires, and never use a higher speed than is necessary. The rotor is driven by the pulley " P " which is mounted on the spindle " SP," and the bearings which control this spindle are mounted in a micrometer head " MH " which enables the clearance between the rotor and the cone " CS " to be adjusted to any degree desired.

When operating the mill the material to be dealt with is fed in through the inlet "I" at a considerable rate; it then passes through the fine film between the conical surfaces, and, owing to the enormous speed of the rotor, the particles of solid suspended in the film are rapidly and effectually torn apart. If two liquids, normally immiscible, are being passed through the film, their particles become so finely divided that they form an emulsion.

The difficulty of making an emulsion with coal tar oil containing anything like 30 per cent. of pitch is well known, but with the aid of this mill an emulsion of this nature can be obtained very readily, an emulsion which can be diluted with water.

One of the most important processes which has been made possible by the "Premier" Mill is that of preserving timber economically by the use of an emulsion of creosote and water.[1] It has been found that by means of an emulsion of creosote and water it is possible to obtain exactly the same depth of impregnation with a fraction of the amount of creosote (depending on the strength of the emulsion used) as is secured in the ordinary way when timber is treated under high pressure with creosote oil. At the same time this new process is far less expensive. In practice an emulsion containing from 30 to 50 per cent. of creosote is used, and it is interesting to note that these emulsions are so stable that they can be boiled or frozen without change of composition, and when they are forced into timber it is found that the emulsion breaks down slowly and uniformly covers the whole of the cells of the timber with an even layer of creosote.

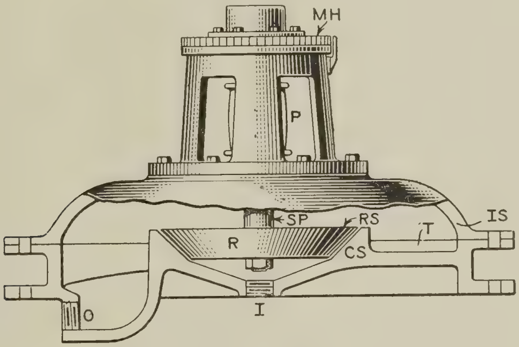

FIG. 94.—THE "PREMIER" MILL.

With the "Premier" mill it is possible to extract tar acids from tar oil by means of caustic soda, owing to the fact that if two or more immiscible liquids be passed through this mill, then these liquids are broken down into such an extremely fine state of division that the area of contact surface is increased thousands of times. Under this condition chemical reaction between the two immiscible liquids is speeded up very considerably. In using this method of extracting tar acids the requisite quantities of tar oil and caustic soda are run simultaneously into the mill, when the reaction takes place at once, and the washed tar oil and carbolate are run away from the plant simultaneously and continuously into a tank where separation takes place. There seems great likelihood of the fact that benzoles and naphthas may be washed with acid or alkali in this type of plant.

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[1] For instance, the "Plexosote" process of Messrs. Burt, Boulton and Haywood, Ltd.

CHAPTER XI

RECOVERY OF CARBOLIC AND CRESYLIC ACIDS

Crude carbolic and cresylic acids are a source of considerable income to the tar distiller, and in all well regulated works every care is exercised to recover the maximum amount of each from the tar distillates in which they exist. These two articles consist of mixtures of phenols, chiefly of the monohydric series, of which phenol, carbolic acid or hydroxybenzene ($C_6H_5 \cdot OH$) is the first. The next in the series are the three isomeric creosols or hydroxytoluenes ($C_6H_4CH_3 \cdot OH$).

Phenol occurs in the form of colourless deliquescent prisms which melt at a temperature of 42·5° C., and turn pink on exposure to light. It boils at 183° C., and can be distilled in a current of steam. According to H. Leroux[1] pure phenol melts at 40·85° C. and boils at 180° C. under 760 mm. pressure. The melting-point of phenol is lowered very considerably by the addition of comparatively small quantities of water. C. T. Bennett[2] gives the following figures: Original phenol melting-point, 40·5° C.; a mixture of phenol and water containing 13·1 per cent. of the latter had a melting-point of 8·5° C.; a mixture containing 16·7 per cent. of water melted at 6·5° C.; whilst one containing 21·9 per cent. of water gave a melting-point of 2·5°–3·0° C. It is concluded by J. Kendall and J. J. Beaver[3] that to determine the specific conductivity of the cresols and phenol is the best means of testing for absolute purity. They give the following constants for the pure materials: Phenol, m.p. $39{\cdot}70° \pm 0{\cdot}02°$ C., specific conductivity at 40° C., $11{\cdot}98 \times 10^{-8}$, at 50° C., $14{\cdot}07 \times 10^{-8}$; o-cresol, m.p. $30{\cdot}60° \pm 0{\cdot}02°$ C., conductivity $0{\cdot}127 \times 10^{-8}$ at 25° C., p-cresol, m.p. $34{\cdot}55° \pm 0{\cdot}02°$ C., conductivity $1{\cdot}378 \times 10^{-8}$ at 25° C., m-cresol, m.p. $11{\cdot}10° \pm 0{\cdot}02°$ C., conductivity $1{\cdot}397 \times 10^{-8}$ at 25° C.

At 0° C. phenol possesses a specific gravity of 1·084, at 18° C., 1·065, and at 33° C., 1·0597. In ether, alcohol, carbon disulphide, benzene, carbon tetrachloride, tetrachlorethane, glacial acetic acid and glycerine, phenol is soluble in all proportions. It is also soluble in the fixed and volatile oils. A mixture of half camphor and half phenol crystals liquefies on standing, with a fall in temperature. On account of the high molecular depression of phenol and the small molecular weight of water a small percentage of the latter (about 8) renders phenol liquid at ordinary temperatures. It is only sparingly soluble in water, 1 part dissolving in 15 parts of water at 16° C. Pure phenol readily absorbs water from the atmosphere, and combines with it to form a definite crystalline hydrate having the formula $2(C_6H_5OH)\ H_2O$. This compound contains 8·74 per cent. of water and melts at 17·2° C. (Allen). With further absorption of water apparently another hydrate is formed, which is liquid. It has the formula $C_6H_5OH{\cdot}2H_2O$ and contains 27·69 per cent. of water. Phenol is not readily soluble in water at temperatures much below the boiling-point. At ordinary temperatures 100 parts of water will dissolve about 9 parts of pure phenol. According to Alexeieff 100 parts of water at 11° C. dissolve 4·83 parts of phenol; at 35° C. 5·36 parts; at 58° C. 7·33 parts; and at 77° C. 11·83 parts. It should be noted that the addition of glycerine to the water increases the solubility. Aqueous solutions of phenol do not react upon blue litmus paper or blue Congo paper.

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[1] *Jour. Pharm. Chem.*, 1919, 20, 88–91.

[2] *Pharm. Jour.*, 1921, 106, 472–473.

[3] *Jour. Amer. Chem. Soc.*, 1921, 43, 1853–1867.

On cooling slowly a phenol-water solution containing about 36 per cent. of phenol, the phenol passes through a colloidal phase, a condition which has been proved by the use of the ultramicroscope.

Aqueous and alcoholic solutions of phenol give a violet coloration with ferric chloride. Phenol possesses the property of coagulating albumen.

According to Pinette the expansion of phenol for the temperature t at 760 mm. is,

$$V_t=1+0{\cdot}000834t+0{\cdot}00000010732t^2+0{\cdot}000000004446t^3.$$

Kopp, however, gives the following:

$$V_t=1+0{\cdot}0006744t+0{\cdot}000001721t^2-0{\cdot}00000000050408t^3.$$

F. Fischer and H. Schrader[1] state that when phenols are heated with hydrogen benzene results. This is shown by the following equations:—

$$C_6H_5OH+H_2=C_6H_6+H_2O$$
$$(a)\ C_6H_4(CH_3)\ OH+H_2=C_6H_5{\cdot}CH_3+H_2O$$
$$(b)\ C_6H_5{\cdot}CH_3+H_2=C_6H_6+CH_4.$$

These workers found that poor yields only were obtained if iron tubes were used, but that good yields were obtained with tinned iron tubes.

According to H. F. Zoller[2] if phenol is slowly distilled in the presence of tin, partial decomposition takes place, some benzene and stannic oxide being formed. This worker obtained from 200 grams of phenol, 30 c.c. of benzene.

Phenol forms compounds with pyridine of the following formulæ: $C_6H_5{\cdot}OH$, C_5H_5N and $(C_6H_5OH)_2$, C_5H_5N. Both substances are, however, in a loose state of combination. Phenol can be converted into cyclohexanol by the addition of hydrogen in presence of a catalyst (nickel).

$$C_6H_5{\cdot}OH+3H_2=C_6H_{11}{\cdot}OH.$$

To melted phenol contained in a pressure vessel is added one per cent. of reduced nickel; the mixture is then heated to between 100° and 120° C., and treated with hydrogen under a pressure of between 10 and 15 kilos per c.m.^{2}, while the liquid phenol is violently agitated.

If phenol in alkaline solution is reacted upon, at a low temperature, with potassium permanganate, it is converted into oxalic acid and optically inactive tartaric acid.[1]

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[1] *Brennstoff-Chem.*, 1920, 1, 4–6, 22–24.

[2] *Jour. Amer. Chem. Soc.*, 1921, 43, 211–212. Also *J.S.C.I.*, April 30th, 1921, p. 253A.

Phenol is used largely in the manufacture of salicylic acid, salol, picric acid, phenacetin, resinous substances like bakelite, and many other important materials.

The three isometric cresols, ortho, meta, and para, occur in commercial cresol or cresylic acid, the proportion of each varying in different samples. Schulze gives the following average figures : m-cresol, 40 per cent. ; o-cresol, 35 per cent. ; and p-cresol, 25 per cent. In water the three cresols are only slightly soluble. At 15° C. 100 parts of water dissolves 2·5 parts of the ortho, 0·53 parts of the meta, and 1·8 parts of the para. Alcohol and ether dissolve the three isomers with ease.

TABLE 58

	O. [1 : 2] Cresol.	M. [1 : 3] Cresol.	P. [1 : 4] Cresol.
M. Pt. (corrected) .	30° C.	3°–4° C.	36° C.
B. Pt. (corrected) .	190·8° C.	202·8° C.	201·8° C.
Sp. gr. . . .	1·0053 at 65° C.	1·0498 at 0° C.	0·9962 at 66° C.

Bromine water converts ortho-cresol into a di-bromo derivative having a melting-point of 56° C., and it forms a picrate melting at 88° C. On adding ortho-cresol to a solution of ferric chloride in water a violet colour is produced.

If ortho-cresol in the form of vapour is mixed with a gas containing oxygen in the presence of a catalyst (a metallic oxide) it is oxidised and yields salicylaldehyde and salicylic acid.[2]

Ortho-cresol is converted into ortho-oxybenzoic acid (salicyclic acid) if reacted upon by alkaline potassium permanganate, and if treated with potassium chlorate and hydrochloric acid yields chloroquinones.

On careful oxidation meta-cresol yields meta-oxybenzoic acid, and if shaken with excess of bromine water tribromocresol is produced. This salt possesses a melting point of 84° C. It also forms a picrate which melts at 88° C., and gives a blue-violet colour to an aqueous solution of ferric chloride.

On adding to para-cresol an excess of bromine water a tetra-bromo derivative is formed possessing a melting-point of 108°, at which point it also decomposes. An aqueous solution of ferric chloride is coloured blue if shaken with a small quantity of this phenol. No chloro-quinones are formed if para-cresol is reacted upon by potassium chlorate and hydrochloric acid. It does not form a picrate. Upon careful oxidation with alkaline potassium permanganate para-oxybenzoic acid is formed.

The cresols can be electrolytically oxidised to the corresponding hydroxy acids, and according to conditions and the extent to which the reaction is pushed a number of dihydroxy derivatives, condensation products or products formed by the disruption of the benzene ring can be obtained.

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[1] Döbner, *Ber.*, 1891, p. 1753.

[2] *U.S.P.*, 1, 380, 277. J. M. Weiss, C. R. Downs and The Barrett Co.

Sodium cresol-sulphonate, when mixed with sodium nitrate in the proportion of thirty-five parts and sixty-five parts respectively, produces a cheap blasting powder.

Trinitrocresol constitutes the substance known as cresylite, which is at times employed as an explosive, alone or mixed with picric acid (trinitro-phenol). It is formed by nitrating meta-cresol (see cresylite tests).

Owing to the presence of the C_6H_5 radicle in phenol the OH group (hydroxyl) possesses weak acid properties (its basic character being somewhat modified). This is shown in its behaviour with caustic alkalies, with which it reacts to form phenolates. One of these which is of importance to the tar distiller is known as sodium phenate, and it is formed by acting upon phenol with caustic soda. It is represented by the formula $C_6H_5 \cdot ONa$, and the reaction is indicated by the following equation :—

$$C_6H_5 \cdot OH + NaOH = C_6H_5 \cdot ONa + H_2O.$$

The hydroxyl (OH) group in the cresols is also weakly acidic in property, but not so strong as in the case of phenol. This is probably due to the modifying influence of the CH_3 group in the $C_6H_4 \cdot CH_4$ radicle. By acting upon the cresols with caustic soda, cresylates are formed having the formula $C_6H_4CH_3 \cdot ONa$. If a mixture of phenol and cresols is treated with insufficient caustic soda to combine with the whole, then a preference is shown for the phenol owing to its stronger acidic property. This fact is used in practice in the recovery of carbolic acid from oils which contain both phenol and cresols. Sodium phenolate and the sodium cresylates are stable in aqueous solution, but are readily decomposed by solutions of mineral acids, hydrochloric acid gas, sulphur dioxide, and carbon dioxide ; and also, in the cold, by sulphuretted hydrogen.

In the process of recovering tar acids from the distillates which contain them, a solution of caustic soda is used as a rule, the strength of which varies somewhat according to the kind of acid to be extracted or the process employed. The caustic soda is sometimes made at the tar works and concentrated by evaporation, and in those works employing the CO_2 process the manufacture of caustic soda (causticising of the spent liquors) is an everyday occurrence. On this account a description of the process of causticising soda ash and spent liquors will be given, before dealing with the recovery processes.

The best quality of soda ash (sodium carbonate) to use is that known as 58 per cent. alkali. This contains on an average 98·75 per cent. of actual sodium carbonate (Na_2CO_3). In the process of converting this material into caustic soda (technically, causticising) quicklime of a high grade is employed ; the best lime for the purpose is white Buxton lime. Theoretically the reaction which takes place is shown by the following equation :—

$$\begin{array}{cccc} Na_2CO_3 + & Ca(OH)_2 = & 2NaOH + & CaCO_3 \\ 106 & 74(56CaO) & 80 & 100 \end{array}$$

In practice it is necessary to use between 10 and 15 per cent. of lime above the theoretical quantity, as the reaction is a reversible one, and, to obtain the best results, the soda-ash solution must be as dilute as possible. Using an ash solution of 20–22° Tw. (1·10–1·11 sp. gr.), the amount of sodium carbonate causticised will be between 95 and 97 per cent. Some prefer to add slaked lime to the ash solution, but in the author's opinion it is far better to employ quicklime and make use of the heat generated during its hydration to assist in the causticising of the sodium carbonate.

The process is carried out as follows: Water is run into the causticiser until it reaches within a few inches of the bottom of the lime grid. Open steam is turned on as soon as the coil is well covered, and steam is allowed to pass during the remainder of the time of charging, and until the water practically reaches its boiling-point. The desired amount of soda ash is added to the water, commencing as soon as signs of ebullition appear, care being taken not to add more ash than is necessary to give a specific gravity of 1·11 (22° Tw.) at 60° F. It is an easy matter to calculate this amount for any size of causticiser, once and for all, from the figures obtained by carrying out a small experiment in the chemical laboratory. The ash solution should cover the bottom bars of the grid about 1 inch, and while at a temperature of approximately 198° F. the lumps of caustic lime should be thrown into the grid, a few shovelfuls at a time, until the calculated quantity has been added. Let each lot of lime " break down " and wash out of the grid before adding a further quantity, and keep the agitator running slowly all the time. For a causticiser containing about 1,200 gallons this operation should take about 15 to 20 minutes. As soon as all the lime has been added, shut off the open steam, put on the closed steam, and increase the speed of the mechanical agitator a little. After about 1½ hours it is well to remove a sample and test it to see how the causticisation is progressing. It generally takes about 1½ to 2 hours after the lime has been added to complete the operation. This time may be shortened a little if a large excess of lime is used, for instance, 110 lbs. of lime to every 100 lbs. of soda ash used.

When the causticisation is complete, the contents of the causticisers are allowed to remain at rest for about 3 hours, and then the clear caustic soda removed by a skimmer pipe to the storage tank; as much as possible of the caustic soda solution should be run off. To the mud or sludge is now added some cold water, the volume depending upon the quantity; if 10 cwts. of soda ash have been causticised, then about 250 gallons of water will be sufficient. Open steam is turned on and the agitator started, and both the passage of steam and the agitation are continued until the contents of the tank begin to boil. One hour is allowed for settling, and then the clear liquor is run direct to the evaporator, any milky liquor being passed through the filter first. A further 250 gallons of cold water are added to the mud, and well mixed in by mechanical agitation only, after which about one hour is allowed for settling, the clear liquor is skimmed off for evaporation, and the soft mud then run on to the filter. The liquid which filters through is evaporated down and then added to the strong caustic soda with the other concentrated washings. By this method of washing it is possible to reduce the content of actual caustic soda ($NaOH$) to 0·5 per cent. If it is desired to dry the mud further, it may be transferred from the filter to a special centrifugal machine.

Recently a method of dealing with waste lime slurry or sludge from causticising plants has been patented and put upon the market under the name of the "Christie" Patent Vibratory Process.[1] All those who have had any dealings with the manufacture of caustic soda and the disposal of the caustic sludge will appreciate the difficulty of getting rid of this waste material, owing to the fact that it retains with great tenacity a very large percentage of water, varying in amount between 42 and 55 per cent. Material in a state like this is not easy of transport to a tip; there is a liability of leakage from the tip carts on to the roads, causing road fouling, and the consequent imposing of penalties. Also considerable difficulty is found in arranging with the owners of tips to allow such wet material to be dropped upon their land.

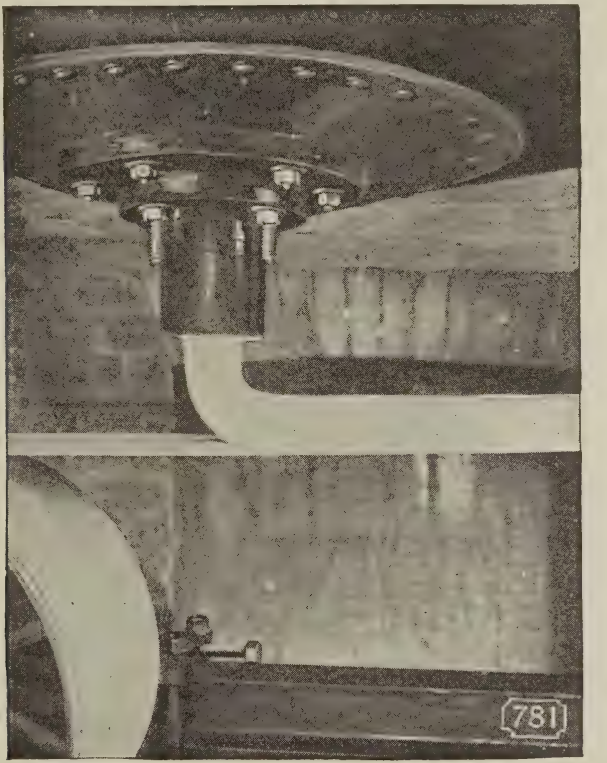

Fig. 95.—Lime Sludge coming away from bottom of Christie Patent Vibratory Vessel

As already pointed out, centrifugals will further dry this material, but will not remove the entire quantity of water, and under these circumstances the usual place of disposal is the tip.

There is to a large extent a market for the absolutely dry caustic sludge, particularly in the agricultural industry, and it is possible by the "Christie" process to produce an evenly powdered carbonate of lime in a form which makes it not only acceptable to the farmer for even distribution on the land, which is important, but allows the use of mechanical distributors. The discovery was made by Mr. H. W. Christie that when caustic sludge is subjected to vibratory influence it is converted into a viscous fluid without requiring an additional quantity of water. The process is carried out briefly as follows :—

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[1] The plant to carry out this process is manufactured only by Messrs. Ernest Scott & Co. of London.

The sludge is first dehydrated as far as possible by the use of vacuum filters (a filter as described on page 219 would be suitable), then discharged into a large receiver fitted with the necessary apparatus to produce the vibratory effect. This piece of apparatus is surprisingly simple in character and absorbs rather more than ½-horse power for an output of one ton per hour. At the bottom of the receiver there is fitted a suitable orifice, and from this the sludge flows in a continuous cylindrical tenacious stream (see Figs. 95 and 96). Immediately upon leaving the orifice it is picked up by a belt conveyor of a simple type, upon which it lies and maintains its initial formation. The conveyor carries it directly into a cylindrical rotating drier.

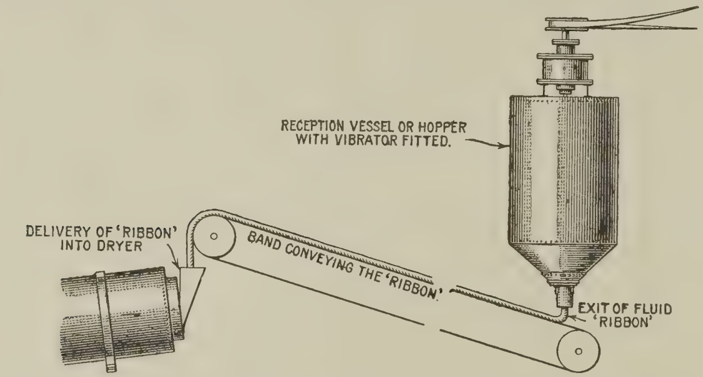

FIG. 96.—DIAGRAMMATIC ILLUSTRATION OF THE CHRISTIE PATENT VIBRATORY PROCESS FOR DEALING WITH SLUDGE PASTES.

It is interesting to note that although the receiving vessel is fitted with a permanently open discharge, the flow stops immediately the vibratory apparatus is shut off. The cylindrical form in which the caustic sludge enters the drier is maintained during its progress through that machine until it becomes dry enough to bring about complete disintegration, and this fact in itself prevents the undesirable condition known as "balling" taking place.

The following gives a typical analysis of sludge before and after treatment :—

	Before.	After.
Calcium Carbonate	47·0 %	97·62 %
,, Hydrate	8·0 %	Nil
Sodium Carbonate	0·20 %	0·82 %
,, Hydrate	0·50 %	Nil
Alumina and Oxide of Iron	0·20 %	0·35 %
Silica	0·10 %	0·17 %
Water	44·0 %	1·00 %
	100·00 %	100·00 %

Before causticising the "spent liquor," which is separated from the tar acids at the divider tanks, it is necessary to bring it up to a standard strength by adding soda ash. The quantity of ash it is necessary to add is found by submitting a sample of the spent liquor to analysis. A good standard to work to is 10 grams of ash per 100 c.c. The amount of ash required to bring the "spent liquor" up to strength being added, causticisation and the washing of the lime mud are carried out in a similar manner to that just described. With reference to the amount of lime to be added, the author has obtained the best results by using 6 to $6\frac{1}{2}$ cwts. of best Buxton lime for every 10 cwts. of actual soda ash in solution in the "spent liquor." It is not possible to gauge the strength of the "spent liquor" by means of a hydrometer, as it contains impurities which affect the specific gravity. Caustic soda for washing out cresylic acid is often made a little stronger, and this necessitates reinforcing the causticised "spent liquor" by the addition of some strong caustic soda solution, or by evaporation, this latter operation naturally raising the content of caustic soda by reducing the quantity of water. Unfortunately, evaporation increases the percentage of impurities, and if this gets large the reaction between the tar acids contained in an oil and the caustic soda in the liquor is somewhat retarded.

Crude carbolic and cresylic acids are extracted from crude naphtha, light oil, carbolic oil, or light creosote. The methods of dealing with these distillates before extracting the tar acids vary more or less in different works. Sometimes the oils are submitted to distillation first, separating into two or three fractions; at other times a portion of the tar acids is washed out of the oils, after which they are distilled and the distillates washed for tar acids. Circumstances determine which process is carried out and also the number of fractions made, and their cut points. Whichever process is used the tar acids are washed out with caustic soda lye, and recovered by either the CO_2 or sulphuric acid method.

Before the oils are washed with the caustic soda lye they should be allowed to settle in the washer for a short time in order to settle out any entangled ammonia water. This material will not only dilute the lye, but as it generally contains ammonium sulphide a reaction will take place, resulting in the formation of sodium sulphide and ammonium hydrate; the former compound is of doubtful value, for if it does combine with certain of the tar acids sodium hydrosulphide is formed during the reaction, and this means a reduction in the active strength of the lye and adds to the amount of impurities which are gathered up during the process. During the settling-out process, any oil which separates naphthalene ("salts out") must be kept warm by means of a closed steam coil, and it is also necessary to wash this type of oil at an elevated temperature. This temperature must not be too high, and if the caustic lye is used hot the same precaution must be taken. If the oil or lye is too hot the amount of tar acids extracted is not so great as when it is warm or cold. Also, if the process of interchange is being carried out and the carbolate or oil is at too high a temperature there is a tendency for the carbolate to give up some of its tar acids to the oil. A good "average" temperature to use when washing is 85° F. It should be borne in mind that the caustic soda lye must not be too strong.

The method of interchange is employed in both the CO_2 and sulphuric acid processes. It consists in adding a phenolate containing a little carbolic and much cresylic acid, or all cresylic acid, to an oil rich in carbolic acid, when the carbolic acid in the oil displaces the cresylic acid in combination with the soda in the phenolate, the cresylic acid going into solution in the oil. Interchange takes place.

If the tar acids are to be recovered by the sulphuric acid process, the fresh, or "clean," caustic soda lye used for the purpose of washing an oil is moderately strong, varying in specific gravity from 1·150 to 1·225 at 60° F. The specific gravity of "clean" lye used in the CO_2 process varies between 1·110 and 1·140, but that from "spent liquor" generally has a much higher specific gravity (at times 1·150), due to impurities in solution. Sometimes "clean" lye is used to wash a fresh oil, and with reference to the amount of caustic lye required, this will vary according to whether it is desired to take out the whole of the tar acids or only a portion. By testing the oil for its content of tar acids, and using the chemical equation given on page 229, or by adding measured volumes of lye to a known quantity of oil until no further decrease in bulk takes place, the chemist can determine approximately how much lye to use.

In following through an interchange process, using moderately strong lye at the finish, it will be assumed that the phenolate with which it is desired to wash the fresh oil stands at a specific gravity of 1·110 and contains 21 per cent. of tar acids possessing a crystallising point of 60° F.

It is not possible to give detailed figures with reference to the amount of phenolate to be put on an oil; this will vary according to the quantity of oil it is required to wash and also with the kind of oil. The amount must, therefore, be determined by experiment in the chemical laboratory. After the oil has been washed with the phenolate containing 21 per cent. of tar acids, it is allowed to settle for a short time, say, about half an hour; the phenolate is then run off to a storage tank, tested, and retained for further use. The oil is then washed with another phenolate containing, say, tar acids of a crystallising point of about 58° F. With a good oil the crystallising point of the tar acids in this phenolate will be probably raised to about 60° F. A further settling of the oil and phenolate is allowed to take place and the phenolate removed to a storage tank, or if desired into the tank containing the phenolate which has in solution the higher crystallising acids. The oil may now be washed with another phenolate containing tar acids possessing a crystallising point of, say, 45° or 50° F. The crystallising point of these acids will probably be increased to 50° or 55° F. A settling is allowed, as already described, and the phenolate removed. Sometimes the oil is now washed with a strong solution of caustic soda, the specific gravity of which may be 1·175 at 60° F. The resulting phenolate is, as a rule, used on a fresh oil. If the oil be particularly rich in crystallisable acids, a further wash with phenolate may be given before using caustic soda lye; and in this connection it is urged that tests be made in the chemical laboratory throughout the whole operation of washing.

The following particulars relative to washing oils for crude carbolic only or for crude carbolic and crude cresylic will no doubt prove useful to the student. They are taken from actual works practice.

Crude Naphtha.—Washed free of tar acids (total extraction): 1,000 gallons of oil taken.

350 to 450 gallons of caustic soda lye at 22° Tw., or equivalent in active strength, if for CO_2 recovery process, or at 30°–35° Tw. if for sulphuric acid recovery process. Resulting phenolate reserved for interchange.

Light Oil.—Washing for carbolic only (*a*): 3,000 gallons of virgin oil taken.

1*st wash.*—1,000 gallons caustic soda lye (7·6 grams NaOH in 100 c.c.). Resulting phenolate sent direct to CO_2 carbolic recovery plant.

2*nd wash.*—600 gallons caustic soda lye (7·6 grams NaOH to 100 c.c.). Resulting phenolate sent direct to CO_2 recovery plant.

3*rd wash.*—1,000 gallons weak phenolate off once distilled light oil or off crude naphtha or virgin light oil.

Test resulting phenolate. If phenols low in crystallising point use for interchange on light creosote, if crystallising point suitable run phenolate to recovery plant.

4*th wash.*—1,000 gallons weak phenolate.

Resulting phenolate to be used for interchange.

After the four washes distil the light oil. The distillate, known as "once distilled light oil," is washed with clean caustic soda lye until free from tar acids, and the resulting phenolate is kept for interchange purposes.

2,000 gallons once distilled light oil for washing.

1,000 to 1,500 gallons caustic soda lye added according to the amount of tar acids present.

Note.—If using the sulphuric acid recovery process the caustic soda lyes are used stronger and correspondingly less in volume.

Light Oil.—Washing for carbolic only (*b*): 3,000 gallons of virgin oil taken.

1*st wash.*—1,600 gallons weak phenolate off light oil, crude naphtha or once distilled light oil.

Resulting phenolate reserved for interchange.

2*nd wash.*—1,600 gallons weak phenolate as used for 1st wash.

Resulting phenolate to be used for interchange, say, on light creosote (or carbolic oil).

Note.—After this wash treat the light oil as in example (*a*) 3rd wash, above.

Light Oil.—Washing for carbolic and cresylic (*a*): 3,000 gallons of virgin oil taken.

1*st wash.*—1,000 gallons of caustic soda lye containing 7·6 grams NaOH in 100 c.c.

Resulting phenolate sent direct to CO_2 carbolic recovery plant.

2*nd wash.*—600 gallons caustic soda lye (7·6 grams NaOH to 100 c.c.).

Resulting phenolate sent direct to CO_2 carbolic recovery plant.

3*rd wash.*—1,000 gallons moderately weak phenolate from interchange carbolate boiler.

Resulting phenolate if crystallising point of tar acids suitable sent to carbolic recovery plant, if crystallising point still too low use for interchange again.

4th wash. Each of 1,000 gallons caustic soda lye at 30° Tw.
5th wash. Resulting phenolate sent to cresylic recovery plant (CO_2 process).

Notes.—(*a*) Some distillers prefer to send the light oil to the still with about 4 per cent. to 6 per cent. tar acids left in, and then wash the once distilled light oil as already described. (*b*) If the sulphuric acid recovery process is used the clean caustic soda lye may stand at 35–40° Tw., and correspondingly less in volume is required.

Light Oil.—Washing for carbolic and cresylic (*b*): 3,000 gallons virgin oil taken.

1st wash.—800 gallons caustic soda lye (7·6 grams NaOH to 100 c.c.).

Resulting phenolate sent to CO_2 recovery plant or to interchange phenolate boiler according to crystallising point of tar acids.

2nd wash.—800 gallons caustic soda lye (7·6 grams NaOH to 100 c.c.).

Resulting phenolate dealt with as that from 1st wash.

3rd wash. Each 1,000 gallons caustic soda lye at 30° Tw.
4th wash. Resulting phenolate sent to cresylic recovery plant (CO_2 process).

Note (*a*).—Test oil, and if not free of tar acids put on more caustic soda lye according to requirements.

Notes (*b*) and (*c*).—See notes (*a*) and (*b*) under light oil washing for carbolic and cresylic above.

Middle Oil.—Washing for carbolic only: 3,000 gallons oil taken.

1st wash.—1,000 gallons caustic soda lye (7·6 grams NaOH to 100 c.c.).

Resulting phenolate sent to CO_2 carbolic recovery plant.

2nd wash. 500 gallons, caustic soda lye (7·6 grams NaOH to 100 c.c.).

Resulting phenolate sent to carbolic recovery plate (CO_2 process), or 800 gallons caustic soda lye (strength as above).

Resulting phenolate reserved for interchange on light oil.

Middle Oil.—Washing for carbolic and cresylic acid: 3,000 gallons oil taken.

1st wash. 1,000 gallons caustic soda lye at 7·6 grams NaOH to 100 c.c.

Resulting phenolate sent direct to carbolic recovery plant.

2nd wash.—1,000 gallons caustic soda lye, strength as in 1st wash.

Resulting phenolate used for interchange on light oil, and then sent to carbolic recovery plant (CO_2 process).

3rd wash. 1,100 gallons caustic soda lye at 30° Tw.

Resulting phenolate sent to cresylic recovery plant, CO_2 process.

4th wash.—1,100 gallons caustic soda lye at 30° Tw.

Resulting phenolate sent to cresylic recovery plant (CO_2 process).

Note (*a*).—Test oil to see if it requires any more caustic soda lye.

Note (*b*).—If the sulphuric acid recovery process is used, lye of 35° Tw. may be used for the carbolic extraction, and 45° Tw. for the cresylic acid extraction, and a less volume will be required in each case.

With reference to manufacturing costs it is not possible to give any but average figures, as the cost of raw materials and labour vary from time to time, and in different parts of the country. The average pre-war cost for labour and chemicals to produce 1 gallon of 60° crude carbolic acid by the CO_2 process was 1·62d., and if carbolic and cresylic CO_2 recovery plants were worked together the average cost for labour and chemicals to produce 1 gallon of 60° carbolic was 1·48d., and 1 gallon of 97–99 per cent. cresylic, 1·60d. The pre-war cost of producing 1 gallon of tar acids by the sulphuric acid recovery process average out at about 4d., this high figure being due to the fact that all the caustic soda is wasted, and a larger volume of B.O.V. is required than in the CO_2 process.

Table 59 gives the results of some works experiments on washing oils which may prove useful to students.

TABLE 59

Oil.	T. A.	Wash.	Carbolic.		Caustic soda lye (7·6 grams NaOH per 100 c.c.)
			Water.	Cryst. pt.	
	Per Cent.		Per Cent.	F.	Gallons.
Light oil, 3000 galls.	27½	—	—	—	—
	22	1st	14·5	76°	1,000
	18½	2nd	12·5	67°	600
	15	3rd	13·0	60·5°	600
	12	4th	15·0	47·5°	500
	9½	5th	15·0	32·0°	200
Crude naphtha, 1,000 galls.	6	—	—	—	—
	0	1st	14	39·5°	400
Middle oil, 3,000 galls.	20	—	—	—	—
	15	1st	14	64°	800
	12	2nd	13·5	55°	350
Re-distilled light oil, 1,550 galls.	22	—	—	—	—
	16	1st	14	not at 28°	400

In all the washing processes care must be taken not to agitate too vigorously or too long, as there is a possibility, if this is done, of forming undesirable emulsions which may take several hours to separate. Some of the lighter tar distillates, such as crude naphtha, once run light oil, and sometimes even virgin light oil are washed entirely free of phenolic bodies, and there are cases when even a light creosote is served in the same way. At times, however, virgin light oil and light creosote are only partially washed for tar acids and then submitted to distillation. It is sometimes preferred to distil the light oil and light creosote previously to washing for tar acids. Which of these various methods is used will depend entirely upon the circumstances existing in the works. It should be remembered that an oil containing a fair amount of naphthalene will deposit that substance in the washer very freely after the tar acids have been washed out.

It is found by experience that tar acids assist materially in holding naphthalene in solution in tar oils, and this is due to the greater solubility of naphthalene in phenols than in coal tar hydrocarbons. It is necessary, then, in cases of salty oils, to keep them at a temperature above that at which the naphthalene contained therein will crystallise out. As the majority of tar distillers manufacture crude carbolic and cresylic acids, it is necessary to run those phenolates which contain tar acids which do not crystallise at, say, about 35° F., into special tanks to be worked up for cresylic acid. Only those phenolates which contain crystallisable tar acids are used for the manufacture of crude carbolic acid. The last wash off the light oils, and generally all the washes but the first off light creosotes, are used for the manufacture of cresylic acid.

The next process is to recover the tar acids from the phenolate, and the method used is the same whether the phenolate contains crystallisable acid (carbolic acid) or cresylic acid.

Dealing with the sulphuric acid "springing" process, which generally follows the interchange process just described, the phenolate is run into a suitable tank and diluted with water until its specific gravity reaches 1·08 at 60° F. It is then allowed to rest for an hour or two, in order to allow any oil which may be held in suspension in the phenolate to rise to the surface. This oil is skimmed off, as should it get mixed up with the crude carbolic acid it will reduce the crystallising point, or, on the other hand, should the acids be non-crystallisable (cresylic acid), it will probably bring down their value by increasing the amount of impurity in the finished product.

After the oil is skimmed off, sulphuric acid of about 146° Tw. (B.O.V.) is added carefully, with thorough stirring. The amount of acid necessary to "spring" the tar acids must not be exceeded, and can be found by occasionally testing the contents of the "springing" tank with blue litmus paper. When the contents are just acid to litmus, after a thorough agitation, they are allowed to rest for from six to eight hours. The tar acids are then separated from the sodium sulphate liquor underneath by first of all removing the latter through a bottom drain cock, care being taken that no tar acid escapes during the operation. The sulphate liquor is run to the sewer. When tar acids begin to show, it is as well to allow a further settling of about ten minutes or so, or to run a few gallons through a separator. The tar acids may then be conducted to a storage tank, and tested for strength, prior to mixing with other strengths, or to filling into packages for despatch.

With reference to the strength of the sulphuric acid used, the author prefers to dilute the B.O.V. to about 110° Tw. and to keep the phenolate at a specific gravity of 1·10 at 60° F. If too strong an acid is used ,to "spring" the phenolate, there is a risk of the sodium sulphate crystallising out in the "springing" tank during the settling period, and if this takes place it will make it very awkward when the time comes to carry out the separating operation. Strong acid is also liable to act upon the phenols, forming sulphonic acids ; these bodies being undesirable in either crude carbolic or cresylic acids, as they split up during the refining operation when the material is distilled. The tar acids should be allowed to rest in the storage tanks for two or three days, in order to settle out any entangled sulphate of soda liquor. This is necessary in the case of both carbolic acid and cresylic acid.

It is desirable to clear the storage tanks occasionally of the soda sulphate liquor and sometimes crystals which settle at the bottom. Should crystals form, it is as well to steam the tanks out by inserting a temporary 1-inch steam main into the tank.

Carbolic acid is sold in various qualities, such as 40's, 45's, 50's, 60's, etc., and it is possible by a process of mixing to " build " up any desired quality, either from the phenolates or the " sprung " carbolic acid. A very simple calculation will give the approximate volume required. The mode of calculation as used on " sprung " acid is shown in the following example : Suppose in one storage tank there are 200 gallons of 55's carbolic and in another tank a quantity of 45's acid. It is required to convert the 55's into 50's carbolic ; then—

$$\begin{aligned} 200\times 55+x45 &= 50\,(200+x) \\ x(45-50) &= 200\,(50-55) \\ -x5 &= -1{,}000 \\ x &= \frac{1{,}000}{5} = 200 \text{ gallons of 45's acid are required.} \end{aligned}$$

In the CO_2 process the oils are washed with a caustic soda lye of a strength sufficient to absorb, in the case of carbolic acid, an amount which, when the phenolate is tested, will correspond to about 15 per cent. of the phenolate, and in the case of cresylic acid about 20 per cent. The caustic soda as obtained from the causticisers, if the process is carried out properly (see page 230), will be of sufficient strength to yield a phenolate containing 15 per cent. approximately of tar acids, and, as already mentioned on page 233, if the lye is to be used for the recovery of cresylic acid, it must be reinforced with a little strong caustic soda made with the 77 per cent. solid caustic soda or with the electrolytic liquid. The interchange method may be used in the CO_2 process of recovery, but a little more care is necessary in carrying it out.

Before washing the oils, it is absolutely essential to allow any ammonia water to settle out. This is necessary, as it not only reduces the percentage of active agent (caustic soda) in the lye by dilution, but also by combination with the sulphur which exists in the ammonia water as ammonium sulphide, sodium sulphide being formed. It appears, from the results of a number of experiments made by the author and others, that part of this sodium sulphide is converted into sodium sulphate during the progress of the phenolate through the plant.

In the process under consideration, the phenolate is " sprung," or decomposed, by carbon dioxide (CO_2), which is contained in the gas prepared in one of the furnaces mentioned in Chapter X, page 211. The phenolate passes down the " springing " or reaction tower, over the packing or plates, and the gas from the purifying tower containing the CO_2 entering the bottom of the tower and travelling in an upward direction, comes into contact with the finely divided phenolate and decomposes it. It is unwise to pass phenolate through the tower containing less than 15 per cent.

of tar acids, and the rate of pumping to the top of the tower should be between 1½ and 2¼ gallons per minute. This speed will vary according to the type of tower used and the richness of the gas passing up that tower. It is advisable to use a gas containing not less than 19 per cent. of CO_2, by volume. Cases frequently occur, however, where it is not possible to obtain a gas containing more than 15 to 17 per cent. of CO_2, and in these cases it is necessary to reduce the speed of the pumping to somewhere in the neighbourhood of 1¾ gallons of phenolate per minute. It is very advisable to test the spent liquor as it runs from the separator, to find the percentage of tar acid it contains. The maximum amount allowable for a plant working perfectly is 0·5 per cent., and should this amount be exceeded, then it is time to look round the plant to see whether the gas is poor in CO_2 owing to the furnace wanting recharging, or the charge burning hollow, or due to leaks in the gas main, or whether the speed of the phenolate is above that which it should be. The waste gas leaving the springing or reaction tower must not contain more than 2½ per cent. of CO_2. Care must be taken to prevent oil getting into the reaction tower with the phenolate, and time must be allowed for this to separate in the phenolate boilers.

The temperature of the gas as it enters the reaction tower is a matter for consideration. In passing through the dust separator and purifying tower it is cooled to a large extent, but if its temperature be too high or too low the efficiency of the plant will be reduced; a satisfactory temperature is round about 100° to 110° C. in the summer time and about 140° C. in the winter. If, however, the carbolate is warmed before passing to the tower, during the winter months, then the gas temperature can be that used in the summer time.

In an important paper[1] on the decomposition of carbolates and cresylates by CO_2, C. J. Denbigh finds: (1) That all the cresols are more easily liberated than phenol. (2) That the cresols only differ slightly, m-cresol being the most easily liberated, o-cresol the least easily. These results agree fairly well with the other known combining powers of the cresols. (3) That in the case of both phenol and cresols the decomposition is more complete when warm, and that the rate increases more rapidly with all the cresols than with phenol.

Two papers,[2] dealing with the loss of phenol contained in the waste sulphate liquors of the sulphuric acid process of "springing" carbolate, are worthy of the attention of the student. In order to keep the reaction tower in good working order, it should be steamed out at intervals of about eight weeks.

With reference to the manipulation of the CO_2 furnace, it is advisable to charge this piece of apparatus about every four hours, or even more frequently with some types of furnace, and in all cases to see that hollow places do not occur, and that

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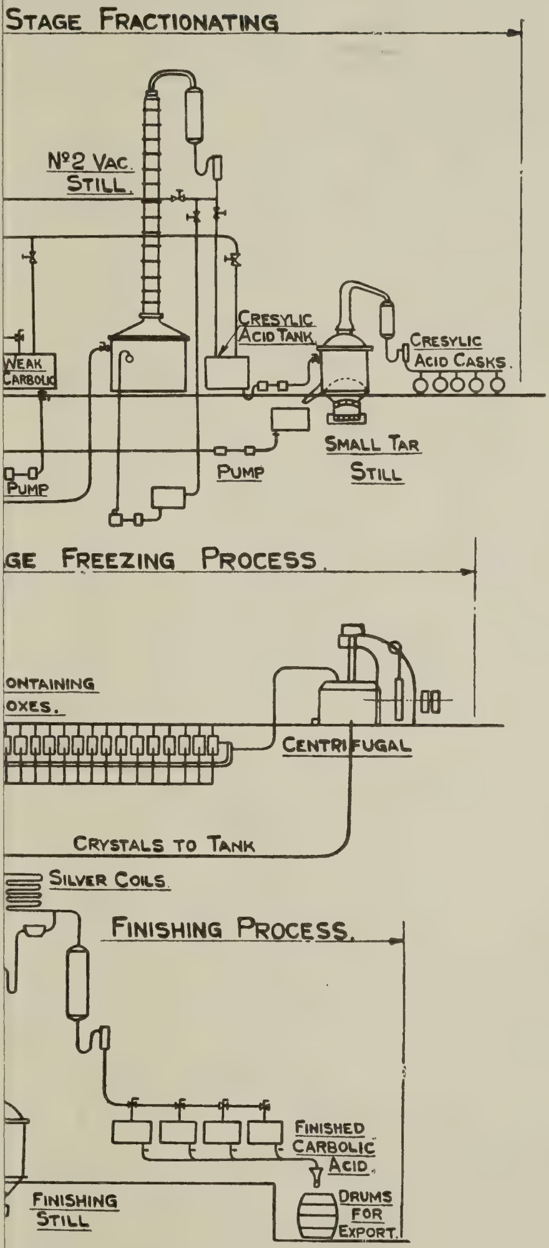
[1] "The influence of Temperature on the Decomposition of Sodium Carbolates and Cresylates by Carbon Dioxide, *J.S.C.I.*, November 15th, 1918, p. 306T.

[2] "Some Observations on the 'Springing' of 'Carbolate' and the recovery of Phenol from the resulting Aqueous Liquor," H. M. Dawson, *J.S.C.I.*, June 15th, 1920, p. 151T.

"Phenol losses in the Decomposition of Phenate Liquors," B Hardman, *Chem. Trade Jour.*, April 30th, 1921, p. 561.



Carbolic Acid.

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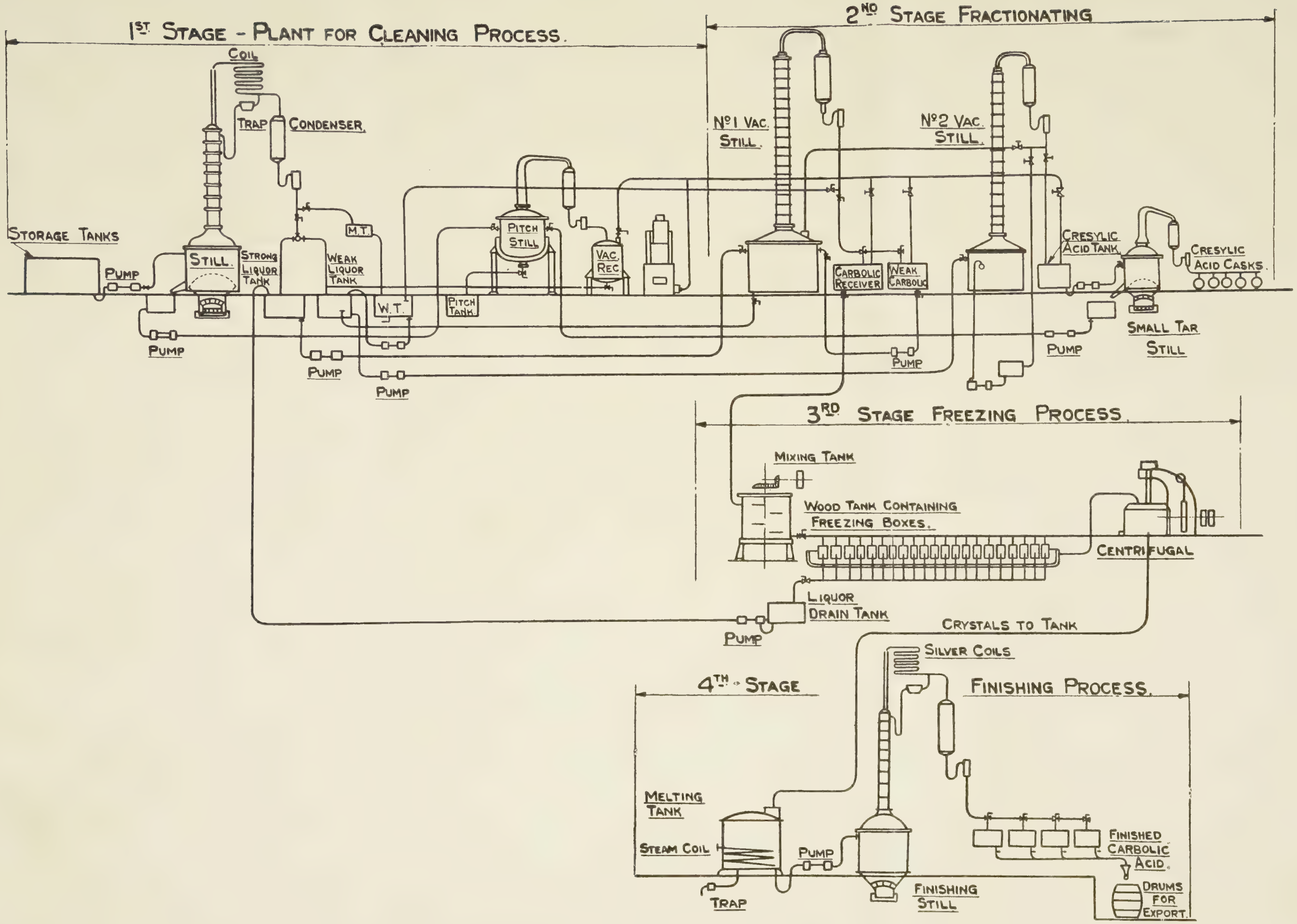

Fig. 97.—Diagrammatic illustration of Blair's Process for Refining Crude Carbolic Acid.

To face page 240.

the contents of the furnace are kept compact. This, of course, can be done by regular inspection, and, if a defect is found, using the poker intelligently. The coke should not be too large, about a size which will pass through a 1½-inch to 2-inch riddle or sieve. It must be of the best quality, as free as possible from water, sulphur, and clinker. In some works the gas containing carbon dioxide is produced in a small limekiln, the lime from which is used to causticise the spent liquors (impure sodium carbonate).

The tar acids and spent liquor leave the reaction tower at the bottom and are conducted to the two dividers (see Chapter X, page 209), and here the tar acids are separated from the spent liquor, the latter running to storage boilers, and the former to settling receivers. The tar acids are allowed to stand in these receivers for several hours, to settle out entangled spent liquor, and then run into the finishing tank in measured quantities, for treatment with a small amount of sulphuric acid. It is necessary to use this acid, owing to the fact that a complete decomposition of the phenolate does not take place in the reaction tower. The acid should be added carefully, with thorough agitation, until the mixture changes a blue litmus paper red. In this operation the acid not only decomposes the remaining phenolate, but assists in the removal of some of the water. It is advisable to use a B.O.V. of about 140° Tw. in this operation.

After the sulphuric acid has been added, it is as well to carry out a laboratory test for the crystallising point, if crude carbolic is the quality under treatment, and in any case for the percentage of water. Should the latter be above 15 per cent. it will be necessary to add a little more sulphuric acid to the contents of the finishing tank in order that it may be reduced. When the desired result is obtained, the phenols are best removed to a storage tank by syphoning over into a blow-boiler and transmitting by compressed air.

With reference to the finishing of cresylic acid, it is necessary to remove as much water as possible before transferring to the storage tank or the still charge tank. The reason for this is that water is a difficult material to contend with during the process of distillation. If care be used, a large quantity of the entangled water may be removed by the use of sulphuric acid in the finishing tank.

After the carbolic acid has been allowed to remain in the storage tank for a short time, it is ready for despatch, and is either barrelled direct from the tank or else pumped (or, better still, transmitted by compressed air) into railway tanks or tank boats. Of course, it is necessary that a careful test be made in the chemical laboratory to determine the crystallising point and other constants of the acid before it is despatched, and it is also advisable to keep two large samples, say, of a pint each, in case a dispute arises between the buyer and the seller. The specific gravity of crude carbolic acid varies between 1·050 and 1·065.

Fig. 97 illustrates in a diagrammatic manner a method of refining crude carbolic acid as carried out successfully by Messrs. Blair, Campbell, and McLean, Ltd. The process consists essentially of four stages: 1st, Cleaning; 2nd, Fractionating; 3rd, Freezing; and 4th, Finishing.

First stage.—In cleaning the crude carbolic acid (called liquor for convenience) it is first pumped into stills with concave bottoms, holding a working charge of approximately 500 gallons. Each still is provided with a fractionating column, which is filled with Raschig tubes. The vapour outlet on the top of the column is connected to a 2-inch vertical pipe, and to this is attached a 2-inch coil of six rings with an outside diameter of 26 inches. This coil at its base is divided into two pipes, one which leads to a condenser coil, through which the non-condensed vapours travel and become condensed, finally reaching a receiving tank, and the other to a separator trap which catches the condensed liquor from the coil, or air-cooled dephlegmator, and returns it through a U-pipe to the top of the column; and in falling from this point to the still the returning condensate scrubs the vapours as they rise through the column.

The distillation of the liquor is carefully conducted, the still working at a rate of approximately 60 gallons per hour, and the distillate is allowed to flow into the strong liquor tank or receiver until a crystallising point of about 60° F. is reached. At this point the flow of the condensate is diverted to a second receiver called the weak liquor tank.

The pitch still, which deals with the residue left in the cleaning still, is 5 feet in diameter and 4 feet in depth with a convex bottom and a 2-inch run-off hole in the centre. It is jacketed on the bottom and half-way up the side, steam being the source of heat. The still charge is worked over through the condenser into a receiver under vacuum, and when no further liquor runs from the condenser the operation is stopped, the residue in the still run off through the bottom outlet into the pitch tank, and the distillate run back into the weak liquor tank.

Second Stage.—In this stage the distillates obtained during the first stage are submitted to fractionation in vacuum fractionating stills, of which there are two, No. 1 for the strong carbolic acid, and No. 2 for the weak. The contents of the strong liquor tank (1st stage) are pumped into No. 1 vacuum still, which, like No. 2 still, is steam heated, and the fore runnings, called the water distillate, passed on to a "water tank" for the purpose of "salting." From the change-over point until the carbolic distillate reaches a crystallising point of 80° F., the condensate is allowed to flow into the carbolic receiver, but when this point is reached it is turned into the second or weak carbolic receiver. All the weak liquors crystallising under 60° F. (1st stage) are pumped into No. 2 vacuum still and submitted to distillation, the first condensate constituting all that which crystallises over 60° F. running into No. 1 still, whilst the second portion of the distillate, that which crystallises under 60° F., is returned to the same still, the balance flowing into the cresylic acid receiving tank. The cresylic acid is pumped into a small fire-heated still, akin to a tar still, about 5 lbs. of powdered red lead per 100 gallons of acid added, and then "cleaned" by submitting it to a distilling process, the distillate being conducted into casks and the residue run into a tank, from which it is pumped into the pitch still included in the plant of the first stage of the process.

Third stage.—This is essentially a freezing and separating process. The strong carbolic liquor crystallising at any point over 80° F. is pumped from the carbolic receiver of No. 1 vacuum still (2nd stage) into a mixing tank provided with a mechanical agitator. When this tank is charged with the carbolic liquor 10 per cent. of water is added, and the mixture stirred thoroughly. The phenol hydrate which is formed is run down into cast-iron freezing boxes, which lie in long wood tanks ; there are twenty boxes to each tank. Cold brine, at a temperature of 20° F., is then allowed to flow into the wood tanks and is kept circulating through them for at least twenty-four hours, the actual time varying according to the season of the year. The crystals of phenol which form in the boxes are separated from the mother liquor and then scooped out and charged into a centrifugal machine for the purpose of removing a further quantity of this liquor. The mother liquor from the crystallising boxes, etc., is run into a liquor drain tank and from this vessel pumped into the strong liquor tank of the first stage plant.

Fourth stage.—This stage constitutes the finishing process. After centrifugalising the crystals are removed from the machine and charged into a melting tank fitted with a steam coil. When the charge is quite liquid it is pumped into a finishing still of a very similar design to the still used in the first stage, the most important difference being the use of silver for the construction of the vapour pipe from the separator trap and the condenser coil. This is very necessary in order to prevent any discoloration of the acid. The still charge is worked off slowly, the distillate running into thickly galvanised tanks to each of which is fitted a zinc run-off tap. From these tanks the refined carbolic acid is run, through a glass funnel, into suitable vessels. If iron bottles or steel drums are used they must be thoroughly galvanised, and well cleaned before use, otherwise the acid will become discoloured.

It is policy before submitting cresylic acid to distillation to allow a further period of time for settling, to enable any entangled acid liquor to settle out, which, should it get into the still, would injure it, and also spoil the pitch. Furthermore, the distilled cresylic acid would not be improved by the sulphurous acid set free during the distillation. When the cresylic has settled sufficiently long, it is charged into the still, the fire lighted, or if producer gas is employed, this is turned on and ignited. The heat may be increased rapidly until such time as the dome of the still begins to get hot, when it is advisable to slacken the temperature of the furnace and work carefully until water and tar acids appear at the worm end. The rate of distillation must be carefully regulated, in order to avoid any risk of a boil-over. A mixture of water and tar acids come over first, and this separates, after leaving the collecting box, in the separator described on page 221. If the cresylic acid has been carefully prepared, there will be very little oil in the first runnings. These first runnings consist to a large extent of poor carbolic acid, but in cases where the still is provided with a good fractionating column, it is possible to obtain a fair percentage of a moderately good carbolic acid. When a fractionating column is used, it is essential that no distillate be passed into the column until water discontinues. Immediately this takes place, then the by-pass is thrown out of gear and the vapours conducted into the fractionating column. The point at which the distillate is changed over from carbolic acid to cresylic acid must be determined for each particular batch of acid as it undergoes the course of distillation, and the chemist should receive samples occasionally. A usual method is to catch the carbolic acid fraction into barrels, and then change over to the cresylic acid receiving tank, cutting out the fractionating column at the same time by means of the by-pass. Some prefer to work each still charge to pitch, but this is a dangerous proceeding as a rule, the risk of burning the plates of the still being very great. It is far better to work several charges up to a determined point, running off the bottoms each time into a bottoms storage tank, and when sufficient has accumulated, to make up a still charge and submit to a re-distillation. If the bottoms are particularly rich in cresylic acid, it may be necessary to run off again into a bottoms tank, and so proceed until they become very viscid, when the final distillation is made with the object of working to pitch. The method of procedure must be determined by the chemist, or manager of the works, for his particular quality of cresylic acid. Care must be taken in working to pitch that the distillation is not carried too far. To over-run the point when pitch is formed will produce either pitch coke or an intermediate product which may be termed spongy pitch ; the latter material is dangerous, as it is exceedingly liable to spontaneous combustion immediately the still manlid is removed, and it is also difficult to remove from the still. Pitch coke, on the other hand, is not liable to spontaneous combustion, but it has to be chipped out of the still, and during its formation the plates may become badly burned. Cresylic acid pitch is not of much value alone, and is generally mixed with the large quantities of coal tar pitch in the bays.

A 1,500-gallon charge of well-settled cresylic acid, if worked to bottoms and not pitch, will take about 24 hours to finish. The total yield of crude carbolic acid, possessing a crystallising point of about 46° F., will approximate 9 per cent., that of 98 per cent. quality cresylic acid 60 per cent., water 8 per cent., and bottoms 23 per cent. A mixture of bottoms, when distilled, will yield approximately 80 per cent. of cresylic acid, the balance being pitch and loss.

The cresylic acid as obtained from the still is not ready for sale. Distilled cresylic acid contains H_2S and other sulphur compounds, which give to it a very unpleasant odour, and it is necessary to remove these objectionable compounds before placing the acid upon the market. To remove these compounds the distilled cresylic acid is air blown in the special tank described on page 222. The cresylic acid is transferred from the receiving tank, either by a pump or compressed air, to the air-blowing tank. Air is now passed into the acid by means of an air compressor, or else drawn through it by a steam ejector. The foul air must be dealt with according to the Alkali Act, and therefore should be " burned " or passed through purifiers, and not allowed to escape into the atmosphere. As regards the length of time required to free the cresylic acid from sulphur compounds, nothing definite can be said, but as a guide to the learner, an average figure of three days may be taken. It is necessary for the chemist of the works to rig up a testing apparatus and submit samples occasionally to a very simple test, as described in Chapter XXII under cresylic acid tests.

Crude cresylic acid is usually sold on the basis of 95 per cent. or 97 to 99 per cent. of tar acids, and it is necessary for the chemist to test each batch as finished for this content. The impurities will, of course, consist chiefly of (*a*) oil, (*b*) naphthalene, and (*c*) water. The specific gravity varies somewhat, generally being between 1·042 and 1·055.

If bromobenzene is heated in a closed vessel with dilute sodium hydrate solution under a pressure of twenty atmospheres, sodium phenate is produced. If the solution of this material is acidified, a phenol of high purity is obtained.[1]

Phenol can be manufactured by heating chlorobenzene and sodium hydroxide solution under high pressure in an autoclave.[2] In this process the two materials are pumped under a pressure of 2,500 to 3,000 lbs. per square inch through a coil of hydraulic pipe, which is immersed in a bath of melted sodium nitrate kept at a temperature of about 370° C. By the use of this coil, which acts as a high-pressure autoclave, the process may be made continuous. The sodium phenoxide is discharged from the coil through a regulated needle valve, condensed, and then acidified with hydrochloric acid, which throws up the phenol. This is separated, distilled, and treated in the usual way.

According to F. Fischer and H. Tropsch and P. K. Breuer[3] it is possible to recover phenols, such as phenol-cresols and xylenols, from coal tar oil fractions by the use of sodium sulphide solution. Their process is based upon the following equation :—

$$C_7H_7OH+NaHS=C_7H_7ONa+H_2S,$$

and briefly it is carried out as follows :—

The tar oil is boiled with sodium hydrosulphide after it has received a preliminary treatment with a little sodium sulphide or an alkaline solution, to remove impurities which prevent the extraction of phenols by this process. The hydrogen sulphide which is evolved is employed to separate the phenols from a previous extraction (the equation given above is reversible, hydrogen sulphide liberating cresol from sodium cresylate if passed into it in the cold). After removing the phenols which are set free, the sodium hydrosulphide remaining can be used for treating more tar oil.

H. P. Hird[4] proposes to extract tar acids from coal tar oils by running or spraying a solution of caustic soda into the vapours generated during distillation, the process to take place between the still and the condenser coil. The liquid which condenses is run into a receiving tank and the sodium carbolate or cresylate allowed to sink to the bottom.

It is concluded by F. Fischer and S. Hilpert[5] that it is possible to separate cresols from tar oils by heating these oils to as high a temperature as possible, under pressure, with more than its own weight of water. The water takes up a portion of the cresols, and when the pressure is released and the temperature reduced, separation takes place.

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[1] U.S. Pat. 1,274,394, August 6th, 1918, appl. July 10th, 1916. See also *J.S.C.I.*, June 30th, 1919, p. 405A.

[2] K. Brown, *Jour. Ind. Eng. Chem.*, 1920, 12, 279–280. See also *J.S.C.I.*, June 15th, 1920, p. 397A.

[3] *Brennstoff-Chem.*, 1922, 3, 1–3. See also *J.S.C.I.*, February 28th, 1922, p. 134A.

[4] Eng. Pat. 125,445, August 2nd, 1916, appl. 10,855, 1916.

[5] *Ges. Abhandl. zur Kenntnis de Kohle*, 1917, 1, 267–268.
Chem. Zentr., 1919, 90, 11, 616–617.
See also *J.S.C.I.*, August 15th, 1919, 528A.

A method of purifying cresylic acid is suggested by H. C. Hamilton.[1] His process is to dissolve crude cresol in a solution of sodium hydrate of equivalent alkalinity, and then add sufficient water to dilute the reaction mixture to such that it will contain about 25 per cent. of sodium cresylate. It is necessary to work with dilute solutions, otherwise some of the cresol will be lost in the process. The dilute solution is either boiled, or live steam is blown into it, until all the volatile impurities have been removed. It is necessary during this process to replace any water which may become evaporated. The boiled or steamed solution is allowed to cool, and if any oil separates upon the surface it is skimmed off, whilst should any naphthalene remain unvolatilised this is removed by filtration. The cresylic acid is recovered by decomposing the cresylate with sulphuric acid, the amount added being just equivalent to the alkali originally used. The cresol which separates is dealt with in the usual manner.

Some years ago the author carried out some experiments with a view to purifying cresols, which are somewhat similar to that just described, and which gave good results. The cresylate was diluted to about 15° Tw., and warmed up to a temperature of approximately 100° C., and a current of air led through it. Properly controlled, the whole of the naphthalene and other impurities was driven off, and there was no loss of tar acids.

Some time ago, when working upon cresols with the object of finding new methods of producing water-white cresylic acid, the author attempted to use aluminium condensers and also aluminium stills and fractionating columns, but found that this metal was entirely unsuitable for the purpose. The condensing coil after a time began to leak, and on examination it was found that the cresol had dissolved the metal in various spots, making small holes about $\frac{1}{32}$ inch to $\frac{1}{16}$ inch in diameter. In one case in which an experimental still constructed entirely of aluminium was used, the bottom gave way in a similar manner after about three-parts of the volume of the cresol had distilled off. Experiments conducted under partial vacuum gave the same results.

Williams and Seligman[2] found that aluminium was corroded by phenol even in the absence of moisture.

Recently Dr. A. F. Campbell,[3] of Messrs. Hardman and Holden, Ltd., Manchester, has evolved a method for the separation of practically pure meta- and para-cresols from crude carbolic acid. The process of separation of the two isomers is based upon a preferential sulphonation and finally a fractional crystallisation of the ammonium salts of the two sulphonates.

The most satisfactory and favourable conditions for a preliminary separation of these two isomers by preferential sulphonation may be summarised as follows :

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[1] *Jour. Ind. Eng. Chem.*, 1920, 12, 50–52. See also *J.S.C.I.*, March 15th, 1920.

[2] *J.S.C.I.*, 1917, 409–515.

[3] *Jour. Ind. Eng. Chem.*, 1922, 14, 732–737. See also *Chem. Trade Jour* September 1st, 1922, pp. 252–255. See also *J.S.C.I.*, September 15th, 1922, pp. 661A–662A.

(1) It is essential that the crude product be a mixture of meta- and para-cresols containing no phenol and only a small percentage of ortho-cresols or the xylenols; (2) it is necessary to carry out the sulphonation at a low temperature, preferably at 40° C.; (3) concentrated sulphuric acid, preferably 96 per cent., and less than the theoretical amount necessary for complete sulphonation; and (4) the process of sulphonation is allowed to continue for six hours. Under these conditions only mono-sulphonic acids are formed.

Taking a fraction which consists approximately of 60 per cent. of meta-cresol and 40 per cent. of para-cresol, the proportions used in sulphonation are as follows: To 100 grams of the mixed cresols are added 37·5 grams of 96 per cent. sulphuric acid, and the reaction mixture heated to, and kept at, a temperature of 40° C. for six hours.

The reaction product is poured into water, and, in order to remove non-sulphonated cresols, the solution is, when cold, extracted with benzene. The extracted solution contains a mixture of meta- and para-sulphonic acids, of which about 80 per cent. is the meta-compound.

These sulphonates are converted into their respective ammonium salts, and then subjected to fractional crystallisation. The para-salt is more soluble than the meta-salt; for instance, at 20° C. 100 grams of water dissolve 19·17 grams of the para-salt against 10·84 grams of the meta-salt. The meta-cresol sulphonate is decomposed by adding half its weight of sulphuric acid and the resulting meta-cresol-sulphonic acid split into meta-cresol by the use of steam. The product obtained is of a purity of 98 to 100 per cent. The para-cresol can be obtained by re-sulphonating the residue from the first sulphonation process, using its own weight of 96 per cent. sulphuric acid. The sulphonated portion will consist of a mixture similar to the first sulphonation, but the residue will contain about 80 per cent. of para-cresol. This residue may be further purified by dissolving it in an excess of caustic soda solution, removing the hydrocarbons by the passage of open steam, and finally recovering the cresols from the sodium cresylate by one or other of the usual methods. The cresylate which separates is then frozen under vacuo and drained, and a product finally obtained with a meta-cresol content of 6 to 7 per cent., and a crystallising point of 22·7° C., which is equivalent to approximately 89 per cent. of para-cresol.

CHAPTER XII

PLANT FOR THE RECOVERY OF BENZOLES, NAPHTHAS, ETC.

THE plant necessary for the production of benzoles and naphthas is complicated, and the designs used by distillers and manufacturers of plants are numerous. It is not possible to describe them all in this book, and therefore the subject is dealt with in a more or less general manner.

It is necessary before the light oils are worked up into what are termed "once run" products that they should be washed free from tar acids and pyridine. Washers for the recovery of tar acids are described on pages 201 to 203, and will not need a second description here. With reference to the removal of pyridine, this is carried out in washers made entirely of cast iron, cast iron lined with lead, or wrought iron ; mild steel is frequently used in place of the latter. These pieces of apparatus must be provided with an agitator, and the necessary gearing to manipulate it. The agitator may be of the archimedean screw type or of the paddle type, and in the latter case horizontal paddles should be used in preference to vertical ones. The author considers the archimedean screw or the typhoon (paddle) types of agitators the best kinds to employ. A vertical washer must be covered in at the top, and should be made with a cone or dish-shaped bottom. An outlet for running off the pyridine acid and acid tar should be placed at the apex of the cone, or the lowest portion of the dish bottom, and connected up to lead piping, which, in its turn, is connected to an acid-resisting metal valve constructed of regulus or Narki metals. The position of the washer may be such that it is not necessary to use lead piping at all, but simply to connect the valve direct to the bottom. Paddle agitators of the horizontal type have the shaft running through stuffing boxes, and care must be taken that these are of a good make, otherwise there will be considerable trouble in connection with leaking. This type of agitator is not recommended by the author.

Wood is the best material to use to cover in the top of a vertical washer, but cast iron, wrought iron, and mild steel are sometimes employed. Let in through the cover of the washer is a charge pipe, an acid supply pipe, a water pipe, and also an inspection hole with a wooden cover. With reference to the water pipe, the author prefers to water-wash the contents through the inspection hole, using a piece of flexible hose. By this means the sides of the washing tank can be washed down with water before any agitation is carried out. The advantage of this will be discussed in the next chapter. A few inches above the bottom of the washer an outlet pipe is attached, through which the washed oils are passed into storage tanks or to the stills.

Some tar distillers prefer horizontal washers, but in the author's opinion these are not nearly so satisfactory as the types just described. It is not so easy to run off the acid tar and pyridine acid from a horizontal washer, or to wash the sides down thoroughly. Furthermore, the draining of the pyridine acid and acid tar cannot be carried out so completely. It is absolutely essential to erect washers in an elevated position, and the best results are obtained if the height is such that the washed oils can be run by force of gravity into the storage tanks or still.

There are many works in which one washer is used for both the acid and the soda washes. This is not advisable, as there is a great risk of spoiling the oil during the soda wash. It is far better to erect two washers of the same size and constructed on the same plan, and use one for the acid and first water-washes, and the other for the soda and final water-washes. The acid tar is run to waste, and the pyridine acid into a receiving tank, which is also often used as a storage tank. As the acid tar is often almost solid, it is best to let it run into open-ended tubs or other suitable receptacles for treatment before disposal. When a lot of pyridine acid has to be dealt with and it is desired to work it up for crude pyridine, it is advisable to put in storage tanks—lead-lined wooden tanks are most suitable. Fuller details of these tanks will be given in the chapter dealing with the plant for the working up of pyridine acid for pyridine.

Broadly, there are two kinds of still used in the process of recovering benzoles and naphthas from tar oils. These are known in tarworks' terminology as " blow-over " stills and rectifying stills. The former type may be subdivided into fire-heated and steam-heated. In the case of light oil, and often with crude naphtha, the " blow-over " still is fire-heated, and in many cases it is not provided with a fractionating column, although it is a decided advantage to fit such a piece of apparatus to the still. Another type of " blow-over " still is steam-heated, and in most cases this kind is used immediately before working the oils through a rectifying still. Steam-heated " blow-over " stills and rectifying stills are always provided with fractionating columns, and generally with dephlegmators.

Fire-heated " blow-over " stills are built similar in shape to a tar still, and are constructed of $\frac{1}{2}$-inch mild steel plates. The bottom is built concave, with a rise of approximately 2 feet 6 inches from the horizontal. To the bottom is riveted a channel plate, and this channel plate is also riveted to the shell of the still. It is advantageous to construct the bottom of the still of sketch plates or segments, and connect these to a circular crown plate on top. The dome of the still is built with a rise, the height of which will vary according to whether the dome is to carry the fractionating column or the fractionating column is to be supported upon joists. In the former case a rise of about 3 feet is necessary for a 9-foot diameter still, but in the latter a rise of about 12 inches for the same diameter is all that is requisite. From the point of view of safety in cleaning or repairing a still, the method of supporting the fractionating column on the dome of the still cannot be considered an ideal one. To remove the last traces of benzole or other similar vapours from a fractionating column is not easy, and the risk of a down-draught of vapour taking place exists. The still should be provided with a tail pipe and run-off tap, a safety-valve, a trial or overflow tap, and an inlet stool, to which is connected the charge pipe. A manhole and lid must also be provided. If the fractionating column is not supported on the dome of the still, it is necessary to provide a cast-iron swan neck and connections, in order to conduct the vapours from the still to the fractionating column.

With reference to the fractionating column, this may be constructed either of cast iron in the form of segments, or of mild steel, and is cylindrical in shape. Its diameter will vary a little, but average diameters may be taken as 2 feet 6 inches and 3 feet. In the case of cast-iron columns, each segment will have a perforated plate fitted into it, or cast on it and then drilled. Mild steel columns are fitted with a series of brackets from top to bottom, on which are supported the perforated plates (see Fig. 98). These plates should be roughly about 9 inches apart, and are perforated with $\frac{1}{4}$-inch holes at a pitch of 1 inch. There is also one hole having a diameter of 4 inches cut in each plate. The plates are $\frac{1}{4}$-inch thick, and in the case of a mild steel column its thickness may be $\frac{3}{8}$-inch. If the still is exposed to the weather, a mild steel column is the best to use, as it is less liable to crack owing to atmospheric conditions, such as rain falling on the column during the time that it is working. Better results are obtained if the column is surrounded by a draught screen, built, say, of corrugated iron sheet; in fact, this method should always be adopted in cases in which the still is erected in the open. At the top of the column a cast-iron vapour outlet is fitted, and this is connected in turn to the vapour pipe.

With reference to the setting of this type of still, the method given under the setting of tar stills on pages 137–145 will give the most suitable results.

Steam-heated blow-over stills (Fig. 98) are constructed of mild steel plate of a thickness varying between $\frac{3}{8}$-inch and $\frac{1}{2}$-inch; sometimes $\frac{3}{8}$-inch plates are used for the shell and $\frac{1}{2}$-inch for the ends in the case of horizontal stills. The best types of steam-heated blow-over stills are of the horizontal pattern. With reference to the size of this type of still this will vary considerably according to the amount of material which is to be dealt with, but a good average is 9 feet in length and 7 feet 6 inches in diameter. The still is fitted with a casting, to which the run-off pipe is connected; also an inlet pipe stool; a 1-inch to $1\frac{3}{4}$-inch open steam-pipe inlet, to which is connected a perforated steam-pipe; steam chests; a series of $1\frac{1}{2}$-inch to 2-inch wrought-iron tubes for closed steam—these tubes being covered at each end by the steam chest covers. They can be withdrawn with comparative ease, and should one give way it can be very easily replaced without causing much delay; a manhole of extra large size, provided with a draw-up manlid. Two manholes are better, as the additional one makes it far easier to clear the still of vapours prior to conducting repairs; a safety-valve; and also a gauge of the glass tube or else of the refraction type, in order to indicate the level of the liquid in the still. Sometimes this kind of still supports the fractionating column; in this case a vapour dome, fitted with a baffle, is usually placed near the fractionating column and connected to it by a piece of cast-iron pipe. Fig. 98 illustrates one way of doing this. The fractionating column should be light and preferably made of wrought iron or mild steel of about $\frac{3}{8}$-inch thick ; in fact, the same type of fractionating column as that already described for fire-heated blow-over stills may be used. The number of plates contained within the fractionating column may be between 18 and 22.

If it is desired to do away with the vapour dome and baffle, a swan neck made of cast iron may be used in its stead to carry the vapours into the fractionating column (see Fig. 99). The bottom of the column is connected to a wrought-iron return pipe of 2 inches in diameter, bent in the form of a U-seal, or, if straight, extending almost to the bottom of the still. If a cast-iron column is used, it is advisable to support it on stanchions and joists, but it may be connected either with a swan neck or vapour dome and baffle to the still, as desired. It is necessary to support this type of still on cradles. These may be of cast iron or built of brick or concrete ; the author prefers cast iron, as in his experience these have given the most satisfactory results.

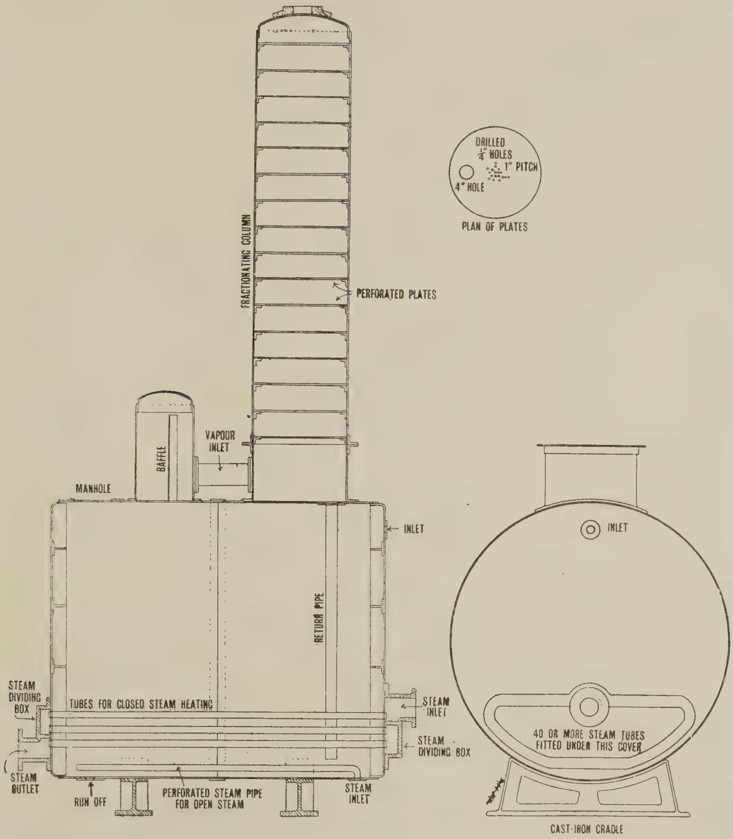

Fig. 98.—Diagram illustrating a Type of Steam-heated Blow-over Still with Fractionating Column. Safety-Valve not shown.

Fractionating stills are generally of the horizontal type, constructed of $\frac{3}{8}$-inch to $\frac{1}{2}$-inch mild steel plates, and provided with fittings of a similar kind to those described for steam-heated blow-over stills (see Fig. 99).

Fig. 100 shows diagrammatically a Blair, Campbell, and McLean benzole still of latest design. The still is constructed of mild steel with dished ends, thus dispensing with a tie rod. It is fitted with a charge cock, safety-valve of the spring type, a manhole and lid of the draw-up type, a sight glass, thermometer, one run-off cock and two sets of closed steam coils. A special feature in regard to these coils

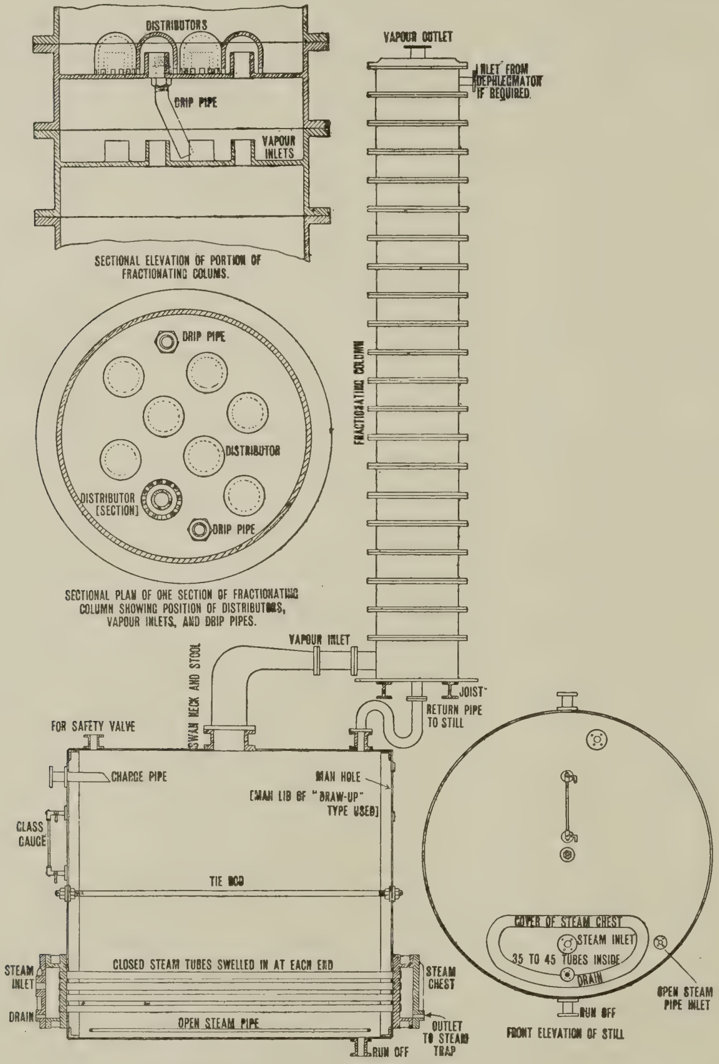

Fig. 99.—Fractionating Still and Column.

is the ease with which they may be withdrawn from the still when any repairs are necessary, without dismantling the still.

Attached to the still direct, but supported by brackets which rest on joists on an upper floor, is a rectifying column composed of cast-iron sections. Each section carries two plates supported on brackets cast on the inside, and one plate which is supported on the flange of the section and constitutes part of the joint between one section and another. The plates are provided with overflow pipes, so arranged that a constant level of liquid is maintained, and are fitted with serrated bubbling hoods.

On the top of the rectifying column is placed a dephlegmator of the tubular type, which is fitted with water inlet and outlet, drain cocks, thermometer, and vapour pipe. It is so arranged that the water surrounds the tubes through which the vapours are passing.

Connected to the dephlegmator by means of the vapour pipe is a special piece of apparatus known as a rectifier, which is supported on brackets resting on an upper floor, or on joists, and which is of the vertical tubular type, in which the vapours surround the tubes whilst the cooling water flows through them. The bottom of the rectifier is connected to a return pipe, which is provided with a U-seal and which enters the rectifying column at the top section. Connected to the top of the cylindrical portion of the rectifier, just under the cover plate, is the vapour pipe which conducts the vapours to the condenser. It is in the rectifier that a further quantity of the higher distilling compounds are condensed, thus purifying the vapours which are ultimately to constitute the distillate.

The condenser is of the coil type, and it will be noticed on referring to the figure (100) that the coil gradually diminishes in diameter from the top to the bottom. This is to allow for the larger volume of vapour in the top coils than in the lower ones and is a good principle. Also if $\frac{2}{r}$ expresses the ratio between the surface exposed to the cooling water and the volume of the coil (r=the internal radius of the coil), then the smaller the radius of the coil the greater the relative surface exposed. The condenser tank is provided with the usual water inlet and outlet.

To the coil end is attached a pipe upon which is fitted an observation glass, and just beyond this piece of apparatus union is made with the necessary receivers. Each receiver is cylindrical in shape, covered in at the top, and provided with an air cock and inspection hole. There are also fitted to each receiver a sight glass and a run-off cock. By adopting covered-in receivers the dangers of loss of volatile material and that of fire are avoided.

Another type of discontinuous rectifying still is illustrated in Fig. 101. There are several differences between this piece of plant and the one illustrated in Fig. 100. The still itself is vertical in position or of the pot-still class, the dephlegmator is dispensed with, and the condenser is tubular instead of the coil type.

Reference to the diagram will show how the steam-heating tubes are arranged on the still bottom, and also the position of the other fittings.

The rectifying column is built up of cast-iron sections, in which are suspended, at regular intervals, trays, which are fitted with bubbling hoods and overflow pipes.

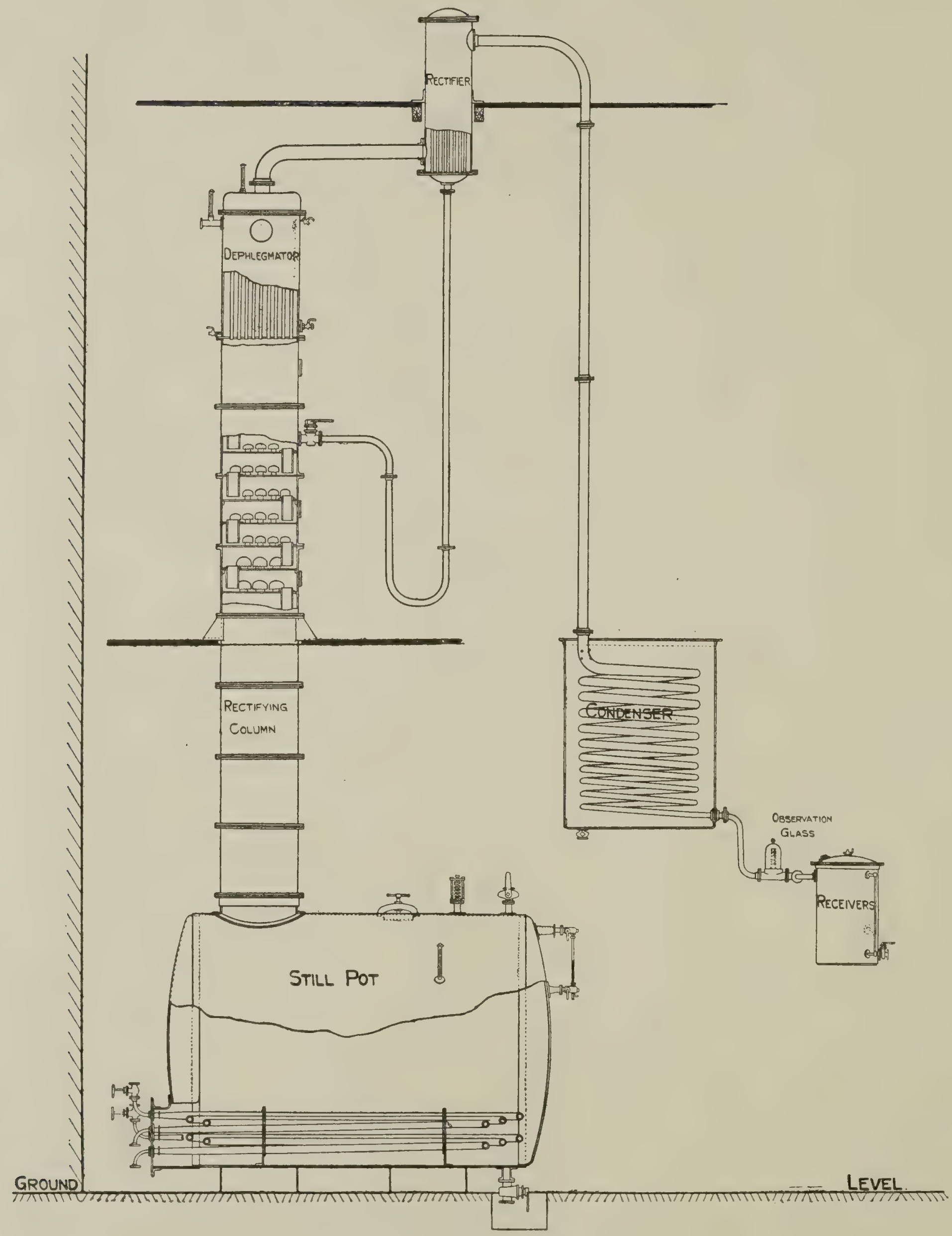

Fig. 100.—Blair's Benzole Still.

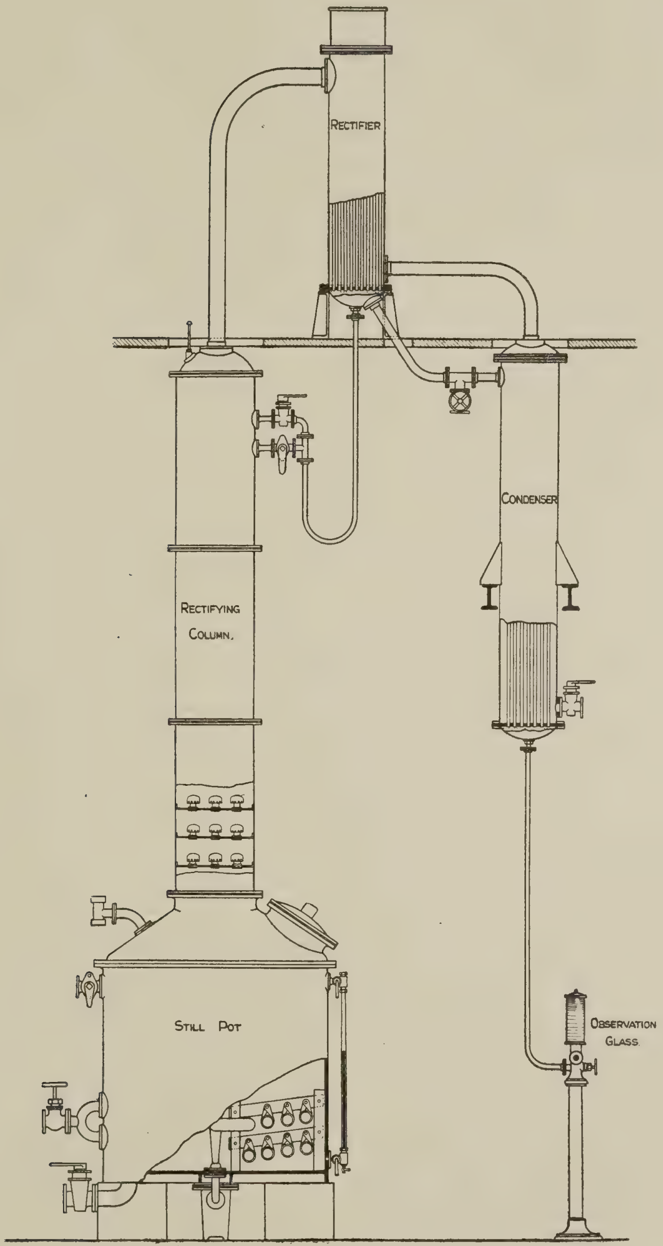

Fig. 101.—Blair's Discontinuous Rectifying Still.

The latter determine the seal for the bubbling hoods, which are so arranged that thorough and intimate contact is assured between gases and liquid. The condensed vapours pass back to the still via these overflow pipes. The bells or hoods are so proportioned that the correct velocity of the vapours is assured, and also the maximum deformation of the vapour bubbles.

The rectifier consists of a number of copper tubes surrounded by an outer jacket, and the arrangement of the inlet and outlet for vapours is such that these surround the tubes whilst water passes through them. The condensate from the rectifier is returned to the top section of the rectifying column by means of the usual U-bend pipe.

In construction the condenser is very similar to the rectifier, only it is much longer. The vapours to be condensed in this case pass through the tubes and the water flows round them.

With reference to the fractionating column, there are a number of types, and it is not possible to describe every one of them in this book. If it is desired to produce ordinary naphthas and benzoles, a fractionating column containing about 22 plates, and having the last six segments water-cooled, will prove quite suitable, but, on the other hand, if it is required to produce benzole, toluole, and xylole, 95 per cent. distilling over within between $\frac{3}{4}°$ and 1°, it is necessary to connect the fractionating column with a separate piece of apparatus known as a dephlegmator. This apparatus, together with condensers, is described later.

Very great care must be taken in choosing a fractionating column for a rectifying still. In the opinion of the author the ordinary perforated plate does not give such good results as those plates which are fitted with special dispersing arrangements, or as those columns which are filled with certain types of packing. Perforated plate columns require a considerable amount of attention in the matter of speed of working, and their limit of flexibility is comparatively small. For efficient fractionation the holes in the plates must be very small and close together; the pressure of the vapour underneath each plate must be greater than the static head of the liquid above, or else the liquid on the plate will drain away; the pressure of the vapour must not become unduly high, or the still operated too fast, as this produces the tendency to lift the seal of liquid off the plate and thus destroy efficient scrubbing action by destroying good contact between vapour and liquid; the plates must be in a perfectly horizontal plane or else the liquid will run to the lower side of them and destroy the seal on the higher side, and the column must be protected against atmospheric conditions as it is sensitive to changes in temperature.

Columns fitted with plates of the bubbling hood or cap and seal type are not anything like so troublesome as those containing perforated plates, and are very much more efficient. A column of this type is described on page 258, and illustrated in Fig. 99, page 252. The flexibility of this kind of column is comparatively great, it can be worked at several speeds without losing efficiency; it is not so sensitive to changes in steam pressure or variations in atmospheric conditions; and owing to the greater depth of liquid on each plate, and on account of the design of the openings of the hoods or caps, and their closeness, the bubbles of vapour are deformed as they escape through the openings, and by impact during their passage through the seal of liquid scrubbing of the vapours is carried out more efficiently.

Among the packed columns of to-day may be mentioned those filled with Raschig, Prym, Goodwin, or Lessing rings. The Raschig ring is simply a piece of thin walled tubing of equal length and diameter, the Goodwin ring is "shaped in the fashion of two hollow truncated circular cones, united at their smaller diameter, at which part both the interior and exterior junction points are rounded and smoothed off, leaving a unit of substantially the same external shape and internal section as a dice-throwing box; but, of course, open at both top and bottom." The Lessing and the Prym rings have a kind of central partition, and on this account they offer a larger contact surface without materially increasing the obstruction to the passage of the vapour and liquid in the column.

The following particulars of Lessing rings[1] will no doubt, prove useful to the reader:—

A fractionating column can be constructed in a very simple manner, by taking a plain mild steel cylinder, fixing a grid near the bottom and then filling up with the rings n irregular arrangement. A column 25 feet high and 3 feet in diameter will require a grid made of 1 inch by $\frac{1}{4}$ inch iron bars placed on edge with 1-inch spaces between them. The bars may be arranged either parallel or concentrically. The object of building a grid in this fashion is not to constrict the upward flow of vapour and downward flow of liquid at this point, and thus counteract the advantage of free space within the rings themselves. The contact surface is large, 1-inch rings giving as much as 70 square feet per cubic foot of column space. Whilst the rings may be regarded as small stills as far as the vapour space is concerned, the large contact surface is chiefly responsible for the excellent fractionating results obtainable. Fractionating efficiency is increased further, due to surface tension effects of liquid forming films along the points or lines of contact between adjoining rings. These films act as more or less effective seals, which are broken by the ascending vapours (to be formed again), and thus ensuring intimate contact and interchange between the liquid and vapour phases. This action amounts to a very considerable bubbling effect, which is increased or decreased with the rate of drip of condensate (reflux).

The amount of column space occupied is small, 1-inch rings occupying only 7 per cent., leaving 93 per cent. free space for gas or vapour and condensate (reflux). This is conducive to reducing back pressure to a minimum, and also permits the use of columns of much smaller dimensions than those usually employed.

The design of the Lessing ring ensures a very high degree of turbulence by reason of the frequent deflection of vapour and condensate streams. Neither will go unbaffled in any one direction for a longer distance than, say, 1 inch. By this is ensured the almost complete release of vapour from solution in the condensate, and close cuts in fractionation are made possible.

The rings, being made of metal, effect a rapid heat exchange between vapour and condensate, and consequently an even distribution of heat throughout the column. It is contended that "channelling" is practically absent when these rings are used, owing to the regularity in the shape of the rings and the irregularity of their arrangement, resulting in an even distribution of liquid and vapour over the whole cross section of the column.

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[1] B. Pat., 139,880, 1919.

The following particulars relating to Lessing rings may be of use to the reader :—

Size of ring	1 in.	$\frac{3}{4}$ in.	$\frac{1}{2}$ in.	$\frac{3}{8}$ in.	$\frac{1}{4}$ in.
Number per litre	40	90	310	700	2,500
Surface per litre in sq. cm.	2,200	2,800	4,150	5,300	8,250
Number per cu. ft.	1,100	2,600	8,800	20,000	71,000
Surface per cu. ft.	70	85	126	163	252
Volume occupied, per cent. of tower space	7	8	9	11	14

As to which is the most suitable column, the packed or the bubbling hood and seal, is a matter of divided opinion at present. The risk of "channelling" exists in the packed column, and if it occurs the efficiency of the column is lowered by a reduction in the amount of contact between liquid and vapour. Metal packing rings, however, assist in the scrubbing action by conducting away the latent heat of vaporisation, which is set free when condensation of the higher boiling products takes place and they enter the reflux liquid, and transferring it to the cooler portion of this liquid which it assists in vaporising. Figs. 102 and 103 illustrate the Lessing ring.

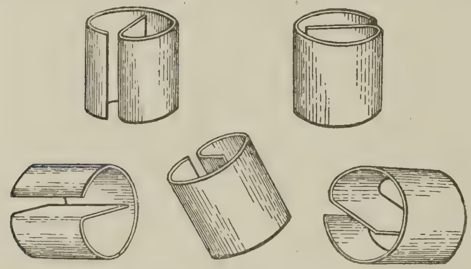

FIG. 102.—LESSING RINGS.

One of the best types of fractionating column which the author knows of is shown diagrammatically in Fig. 99. This column, like most of the columns used for fractionating stills, is built up of cast-iron segments. The number of these segments will vary, of course, according to the degree of fractionation desired. If a dephlegmator is used, a column constructed of between 18 and 22 segments will prove quite suitable, but if it is desired to do without a dephlegmator, it is advisable to build the column of between 25 and 30 segments; the use of a dephlegmator is preferable. The diameter of each segment may vary between 2 feet and 2 feet 6 inches, and the over-all depth between $8\frac{1}{2}$ and 12 inches. The plate is cast on to the body of the segment, and the top of the plate is about 3 inches below the top of the segment. Each plate is provided with eight or more inlets, which conduct the vapours from the lower half of the segment. Over each of these inlets a cast-iron hood or disperser is placed; this disperser is beehive in shape, and has twelve openings $\frac{1}{2}$ inch by $\frac{1}{2}$ inch, as shown in Fig. 99. There are provided also two overflow outlets, to which are connected overflow pipes. The method of arrangement will be seen on referring to Fig. 99. The bottom segment of the column has cast on it a vapour inlet of 4 inches in diameter, and this is connected by a swan neck to the still. There is also cast on this segment a 2-inch connection, to which the return pipe is fitted. The return pipe is passed into the still, and should reach almost to the bottom, or else be bent in the form of a U-seal, as shown in the figure. The top section of the column has a vapour outlet stool cast on it, which may be 2 inches in diameter ; to this is connected the vapour pipe, which will lead either to the condenser coil or to the dephlegmator. If the column is not connected to a dephlegmator, it is very advisable to water-jacket the top six or eight sections. Should the column be connected to a dephlegmator, it is necessary to provide the top section with an inlet hole, to which is fitted the return pipe from the dephlegmator (see Fig. 99). This return pipe is made in the form of a U, with one limb longer than the other, in order to provide a seal of liquid to prevent the vapours from entering the bottom portion of the dephlegmator.

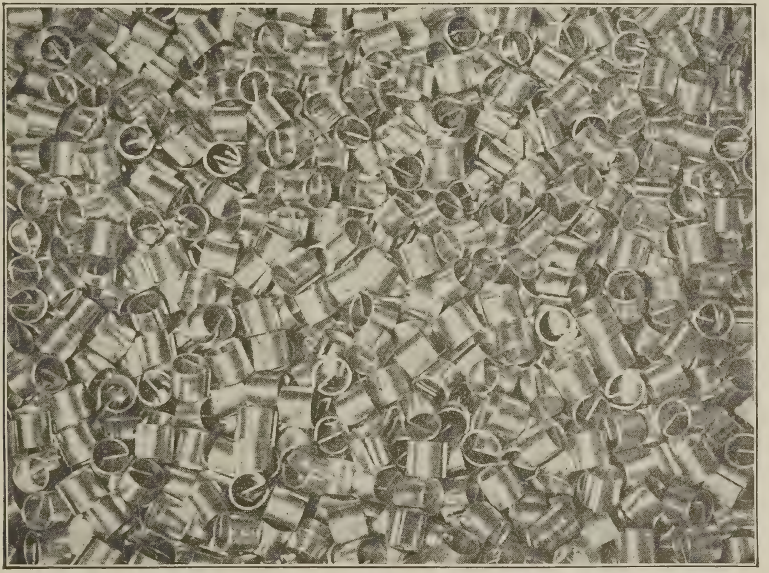

Fig. 103.—Lessing Rings as they appear in position in a Column.

Dephlegmators vary in construction, some being cylindrical, and others square or rectangular in shape. All of these types will give excellent results, but only the cylindrical shape will be described. It consists of a mild steel cylinder, its diameter, as a rule, varying between 2 feet and 2 feet 6 inches and its length between 7 feet and 8 feet. Inside the cylinder, about 1 foot 6 inches from each end, are riveted two plates, into which are fitted a large number of copper tubes of similar diameter (between $\frac{3}{4}$ and 1 inch). Through these tubes a flow of water is maintained, and the vapours from the fractionating column pass round the tubes, the heavier vapours being cooled and returning to the fractionating column via the U-shape return pipe just described (see Fig. 104). The dephlegmator is therefore provided with a vapour inlet at the top, which enters just underneath the top tube plate, and a vapour outlet near the bottom, just above the bottom tube plate. A return pipe is also fitted near the bottom, just above the tube plate. Water is introduced through the inlet fitted to the bottom of the dephlegmator and leaves by the outlet at the top.

After the vapours leave the dephlegmator, or, when this is not used, the fractionating column, they are conducted to a condenser. This condenser may be constructed of wrought-iron tubing, arranged in a number of laps placed in a cylindrical tank, or, especially in cases where a dephlegmator is used, of a cylindrical vessel inside of which are riveted top and bottom plates drilled with holes into which a number of tubes are fitted, very similar in fashion to the arrangements just described under dephlegmators. If it is desired to fit up a condenser coil of the usual type, it is advisable to have it made in one length of wrought-iron pipe. The diameter may vary a little, but one of 2-inch diameter is usually adopted and found quite suitable. The total length of the tube will vary, of course, according to the condition of the

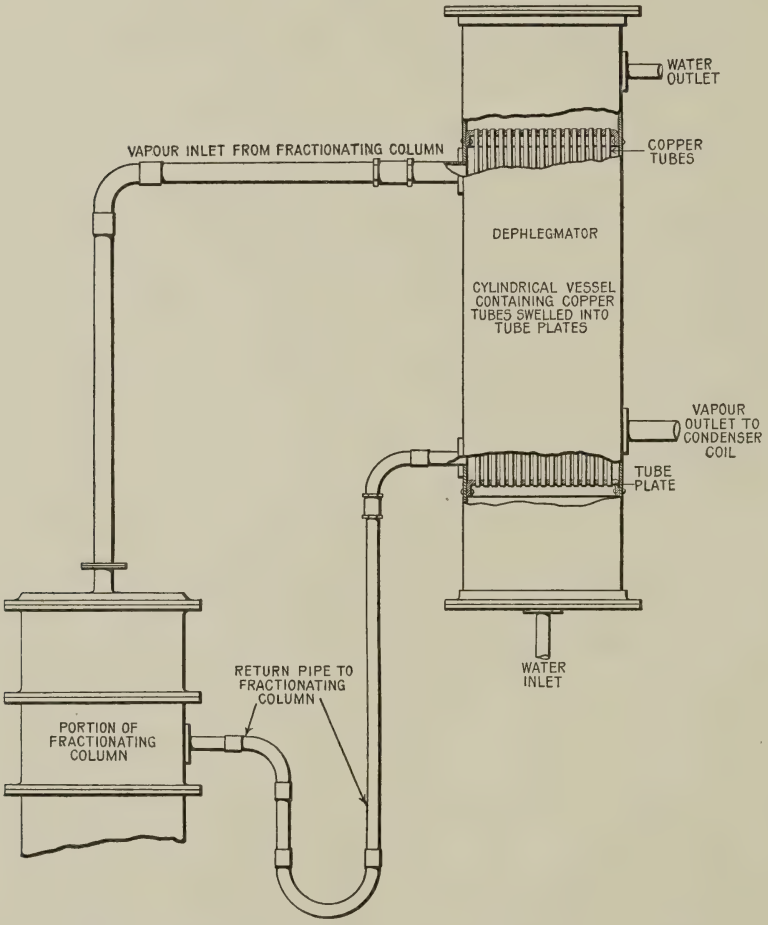
WATER OUTLET
VAPOUR INLET FROM FRACTIONATING COLUMN
COPPER TUBES
DEPHLEGMATOR
CYLINDRICAL VESSEL CONTAINING COPPER TUBES SWELLED INTO TUBE PLATES
VAPOUR OUTLET TO CONDENSER COIL
TUBE PLATE
WATER INLET
RETURN PIPE TO FRACTIONATING COLUMN
PORTION OF FRACTIONATING COLUMN

Fig. 104.—Diagram showing a Type of Dephlegmator and a Method of connecting to the Fractionating Column.

water supply and the rate at which it is required to work the still. With a still working at an average speed of about 70 gallons per hour, 180 feet of 2-inch wrought iron pipe will be quite sufficient. The over-all diameter of each coil may be 4 feet 6 inches to 5 feet, and the distance between each lap should not be less than 4 inches. At least 4 inches must be allowed between the outside of the coil and the inside of the condenser tank, and the top lap of the coil should be covered with about 6 inches of water when distillation is in progress.

The condenser tank is cylindrical in shape and fitted with water inlet and outlet pipes, drain cock, etc., as described on page 153. This incoming water must be released at the bottom of the condenser tank, and is best distributed so that severe eddy currents are not set up and the mixing of the cold water with the hot water in the tank is avoided. Connected to the condenser is a divider box of exactly the same pattern as that described on page 154 (Fig. 49). The outlet from the divider box, however, is connected up to several 1-inch pipes by means of T-pieces, in order to conduct the various fractions to their respective receivers.

Receivers are best when of comparatively small size, cylindrical in shape, and constructed of mild steel plates, the seams being well riveted and caulked. They must be covered in at the top and provided with a connection for the inlet pipe, an inspection hole fitted with a tight lid, an air outlet or air cock, a run-off cock, a drain cock, and a sight glass. As a rule receivers are connected directly to the storage tanks. It is a wise plan to put in one or two spare receivers, in order to be in readiness should occasion demand a special fraction or fractions.

Storage tanks may be square, rectangular, or cylindrical in shape, according to convenience. In all cases they should be covered in and provided with a run-off tap, and also drain cock, through which any water which may settle out can be removed.

In order to avoid fires from the discharge of static electricity it is recommended to ground all apparatus by means of copper wires which must be securely fastened to both the apparatus and a ground wire.

Pipe lines to carry the crude and finished materials are best of wrought iron; those for dealing with sulphuric acid, pyridine sulphate (pyridine acid), acid sludges, etc., should be of lead. Any flange joints should be made with a good jointing material, and the author can strongly recommend a substance called "Permac," which will produce a rustless metal-to-metal joint, quite proof against acids, steam, and solvents, and which presents no great difficulties when occasion requires a joint to be unmade.

The following notes dealing with condenser coils and heating coils will, the author hopes, be of use to students and others. It is not possible to deal fully with the matter of design of these pieces of plant in this book, and for full details the interested reader is referred to the books and papers mentioned in the Bibliography at the end of this chapter.

In the function of cooling as applied to condensing distillates there are two periods, (*a*) that during which the vapour is condensed to the liquid state, and (*b*) that during which the liquid is cooled to a temperature below which it is readily volatilised on standing. In the design of condensers sufficient attention must be given to the factors which will produce satisfactory results in both these periods, and the second period must be considered important and not partially neglected as is sometimes the case. The vapour pressure of the condensate must be reduced, as loss by evaporation is accentuated considerably if the liquid is at a temperature close to its boiling-point.

It is not a simple matter to calculate the size of a condenser as many factors are involved, and some of them are of uncertain magnitude. Robinson[1] tabulates the various factors as under :—

1. The amount of heat which must be removed by the condenser in condensing the vapour.
2. The amount of heat which must be removed by the condenser in cooling the condensed vapour.
3. The amount of vapour entering the condenser from the fractionating column.
4. The amount of inert gas or other non-condensable vapours present in the vapours entering the condenser.
5. The temperature of the vapour entering the condenser.
6. The temperature of the non-condensable gases leaving the condenser.
7. The temperature of the condensed vapour leaving the condenser.
8. The amount of cooling liquid available.
9. The temperature of cooling liquid available.
10. Temperature at which cooling liquid should leave the condensing system.
11. The velocity of vapour by the cooling surface.
12. The velocity of the cooling liquid by the cooling surface.
13. The removal of non-condensable gases from condenser.
14. The physical characteristics of the condensed vapour.
15. The physical characteristics of the cooling liquid.

These factors are fully discussed in Robinson's work.

Whilst the velocity of the cooling water is a factor easily settled, the velocity of the condensate as it flows through the condenser is not known with certainty. The observations of certain workers have led them to conclude that it is seldom more than 3·25 feet per second, and for purposes of calculation the figure 2·6 feet per second is a good average to take, allowing that the cooling surface is covered all over with the condensate. It must not be forgotten, however, that in the case of a coil condenser the condensate wets only the lower and smaller portion of the inside wall of the coil, the upper portion remaining unwetted, and even in the case of vertical tube condensers the whole of the internal surface is not wetted. On this account the calculated cooling surface for coil condensers should be increased by about three times, and that of vertical tube condensers by about twice.

It is a very simple matter to calculate the cooling surface of a coil, or vertical tube condenser, by the use of the formula πdln, where d=diameter of the pipe ;

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[1] See Bibliography at end of this chapter.

l=length of each coil or length of each pipe; and n=number of coils or number of pipes.

The minimum quantity of water necessary for condensing the vapour of a substance and cooling the condensed liquid may be calculated by the use of the formula

$$M=\frac{WL+WS(T-t)}{T_1-t},$$

where

M=weight of water required.
W=weight of substance.
S=specific heat of the substance (liquid).
L=latent heat of vaporisation of the substance.
T=boiling-point of the substance.
t=the final temperature of the condensate (which may be the temperature of the cooling water on entering the condenser).
T_1=the temperature of the water leaving the condenser.

The above formula is for use in cases in which the substance is distilled by fire or closed steam, and when steam distillation is required then a separate, but similar, calculation must be made to give the amount of cooling water necessary to condense the steam and cool the water condensed therefrom. It should be remembered that the amount of cooling water obtained by using the above formula is the minimum quantity, and in general practice would be too small a quantity.

The amount of cooling surface allowed in general practice varies between 1 and 3 square feet for every 1 gallon of condensate cooled to the normal temperature per hour. Although a good factor of safety should be allowed, especially when dealing with highly volatile materials, the author considers the latter figure is somewhat high and therefore not economical, as it will add unnecessarily to the cost of the plant. He has been in the habit of using areas between 1 and 1½ square feet with good results.

In all modern benzole-rectifying plants dephlegmation is practised and water is required in the dephlegmator for the purpose of cooling, as well as in the condenser. It is not quite so simple a problem to calculate the amount of water required in a dephlegmator, the temperature being changed as the several products are worked off. As a guide to the student it may be stated that on a benzole rectification plant the water required for dephlegmation purposes varies from 2 to 3 gallons for each 1 gallon of distillate, and that for the condenser 1¾ to 2 gallons per 1 gallon of rectified distillate. The flow of water through a dephlegmator is best regulated so that a constant difference of about 25° C. is maintained between the vapour and the cooling liquid.

To allow a "dead" space in the centre of a water-cooled coil condenser is not altogether good design as its efficiency is impaired somewhat, due to the formation of convection currents in the water and the consequent raising of the temperature of the colder water at the bottom of the condenser. Although convection currents are to a great extent eliminated if the water is heated at the top, and the passage of heat to the lower portion is excessively slow, the fact must not be lost sight of that a considerable amount of heat is transferred to the cooling water from the material passing through the lower coils of a condenser, say, to about one half-way down, and this will increase somewhat the phenomenon of convection ; and much depends upon the manner in which the cold water is supplied to the condenser tank (see page 153). It is a good plan to fill up the " dead " space by fixing a mild steel cylinder in the tank, with its outer side about 9 inches away from the inner side of the coils, arranging that water does not fill the inside of the cylinder, but air only, and to make the diameter of the laps of the coil as small as possible compatible with the height which can be allowed for the whole condenser. Another method is to put in D-shaped coils, placing two coils together in the condenser tank thus, ᗡD.

With reference to the transmission of heat from the material in the condenser coil to the cooling water, under conditions existing in practice, this is affected to a small extent according to the metal used in the construction of the coil, *e.g.* copper or iron, but to a much greater extent by the films of liquid on either side of the condenser tube wall. This condition is reversed, however, when the thickness of the tube is unduly thick, or the velocity of the cooling medium is *very high*, thus reducing the thickness of the film. Heastie states that a film of water 0·003 inch thick is equivalent, in resisting heat flow, to a copper tube wall $2\frac{1}{4}$ inches thick, or if it is assumed that the average tube wall thickness is 0·08 inch, then the resistance of the metal is only $\frac{1}{278}$th that of the film. In the case of steel the resistance is increased to about $\frac{1}{47}$th.

In the design of the heating coils for a still the chief points to be borne in mind are :—

1. The quantity of heat required per unit of time.
2. The temperature difference between the steam in the coil and the liquid in the still.
3. The coefficient of heat transmission from the steam to the liquid in the still through the metal of the coil.

When heat is transferred from saturated steam to a liquid through a metal (the coil) three resistances present themselves, namely :—

1. The resistance of a film of condensed water (from the steam) on the inner side of the coil.
2. The resistance of the metal of the coil.
3. The resistance of a film of liquid on the outer side of the coil. In connection with the film of condensed water from the steam, the effect of the air which is always present in steam must not be lost sight of.

It has been shown that the greater the length of a metal tube of a given diameter the less is the coefficient of heat transmission, and that for tubes of a fixed length this coefficient decreases as the diameter increases, hence heating tubes should be designed as short as possible and not of too great a diameter.

Steam must not be allowed to become stagnant in the heating tubes ; the more rapid the movement of the steam the greater the heating efficiency. It is also necessary to remove the condensed water formed from the steam as rapidly and as completely as possible in order to keep up the heating efficiency ; the conductivity of water films is very low.

For fuller particulars on these matters the works and papers mentioned in the Bibliography at the end of this chapter must be consulted.

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CHAPTER XIII

RECOVERY OF BENZOLES AND NAPHTHAS

THE various qualities of benzoles and naphthas are obtained from crude naphtha, light oil, and often from light creosote. It is necessary to wash these oils, or certain fractions obtained from them, free from tar acids and pyridine bases before the process of rectification can be carried out, and in the case of the heavier oils, and very frequently with crude naphtha, a first distillation by fire is carried out, as is described below.

Dealing with crude naphtha, this distillate contains chiefly benzene and its higher homologues, and on treatment and rectification yields principally 90's benzole and 50–90's benzole. Crude naphtha as pumped over from the receivers will contain approximately between 4 and 6 per cent. of tar acids and a varying quantity of pyridine bases. The tar acids are removed as described in Chapter XI, page 234. Pyridine bases are not removed until just before the rectification process.

It is preferred by some to submit the crude naphtha to a distillation before washing out the tar acids. Others prefer to wash out the tar acids before distilling, and it depends on the circumstances existing in the works whether this is done or not. In any case, after the tar acids have been removed it is advisable to allow an hour or two for settling, in order that any entangled phenolate may settle out. The extracted naphtha is then submitted to a distillation. This may be conducted in a fire-heated still fitted with a fractionating column, or in a steam-heated still to which a similar apparatus is connected. Two fractions may be collected, the first being run into what is termed the crude benzole receiver, and the second into a receiver for crude solvent. The end of the first fraction is generally found by submitting a portion of the distillate as it runs from the worm end to a rapid distillation in a retort in the laboratory. As soon as the test sample shows the first drop at about 110° C. the distillate is changed over into the crude solvent tank. The end of the second fraction is determined when the specific gravity of the distillate taken from the worm end indicates approximately ·965 to ·970 at 60° F. On to the residue in the still, other material is often placed, or it is removed and kept for working up with heavier distillates at some other time. The methods of obtaining the change-over points just given are not always used; at some works they are determined by readings from a thermometer fitted to the still, and it is sometimes necessary to vary these points according to the requirements which may obtain in the works.

The steam-heated still in which this naphtha may be fractionated must be provided with an open steam coil, as it is necessary to assist the distillation with open steam after a certain point is reached. Generally, open steam is introduced into the still when the distillate at the worm end, on testing in the laboratory, commences to distil at about 95° C. If, however, high-pressure steam is supplied to the closed steam tubes, the open steam may be introduced at a later period or not at all. Care should be taken when first passing the steam into the still not to open the valve too wide. If this is done it will generally cause the still to prime, or, in other words, fill the fractionating column with the heavier material from the still. This, of course, is a serious matter, and will, if it occurs, generally spoil the operation. The valve should be opened very gently at first, say, about one-quarter of a turn, and then the passage of steam gradually increased until the still works evenly. When open steam is introduced, it is necessary to pass the distillate, as it comes from the worm end, through a divider box, in order to separate the condensed steam from the oil. The closed steam is not discontinued during the passage of open steam, but it must be regulated according to the rate of distillation desired.

With reference to washing the distillates for pyridine, this will be dealt with after considering the first distillations of light oil and light creosote.

In dealing with the light oil fraction, this should always be washed with caustic soda lye to remove any crystallisable crude phenol, and also the crude cresylic acid which it contains, before submitting it to a distillation by fire. Some distillers prefer to submit the oil to a fire distillation before washing for tar acids, but this method is, in the author's opinion, a mistake, as some of the tar acids are lost in the bottoms. Details of the methods of washing are to be found in Chapter XI, page 235.

It is absolutely essential, however, to distil the light oil by fire before passing it along to the rectification plant to obtain naphthas. This oil, when distilled in the fire still, which should in all cases be fitted with a fractionating column containing at least 15 plates, may be separated into two fractions and a residue, or one fraction and a residue. The quality of the oil will determine which of these methods is the best to adopt. If the light oil is divided into two fractions, then the change-over point from the first to the second fraction is generally determined when approximately 25 per cent. has come over. With a large number of oils this point is also indicated when the distillate at the worm end shows a specific gravity of about ·925 to ·928 at 60° F. This fraction may be termed " once run light oil A." The second fraction—" once run light oil B "—is complete when the distillate at the worm end shows a specific gravity between ·990 and 1·000 at 60° F. The residue remaining in the still is run to creosote, or to special storage tanks, to await the recovery of the naphthalene. Should it be necessary to remove from the light oil one fraction only, then that fraction is complete when the specific gravity of the oil at the worm end is about ·980 to ·990 at 60° F. In this case also the residue is dealt with as just mentioned.

For the convenience of the still attendant, his " change-over " points, and finishing points, are often given him to read at 100° F. For example, if it is desired to finish the distillation at a specific gravity of 1·000 at 60° F. then the still attendant should stop collecting when his distillate reaches ·980 at 100° F. Open steam is not used during the distillation of light oil by fire.

It is advisable not to work too many charges through the light oil still before submitting it to a cleaning process : ten times may be taken as a good average.

The distillate or distillates obtained from the light oil as just described are now washed free from tar acids, unless they were removed before distilling the light oil, and then submitted to a further distillation, either in a fire-heated or steam-heated still provided with a fractionating column. In this operation the " once run light oil A " distillate may be separated into one fraction and residue, or two fractions and residue. If only one fraction has been distilled off the light oil, this may be separated into one, two, or three distillates and residue.

In the case of the " once run light oil A," if this is separated into one fraction, the whole of it is run into the crude solvent naphtha receiver, and the point at which the distillation is stopped is indicated when the specific gravity at the worm end reaches about ·960 to ·980 at 60° F. When two fractions are made, the first one is mixed with the crude benzole and the second run to crude solvent. The change-over point from the first to the second fraction is determined in a similar manner to that given under the working of crude naphtha on page 266, and the end of the second fraction is found as mentioned above. Considering a case in which only one fraction has been distilled off the light oil, should it be desired to separate this into three fractions, then the end of the first fraction is determined as already described (page 266). The second fraction is stopped when the specific gravity reaches ·940 at 60° F. at the worm end, and the third fraction, which is termed crude heavy naphtha, is finished when the specific gravity of the distillate collected at the worm end reaches between ·960 and ·980 at 60° F.

The " once run light oil B " distillate, if separated into one fraction, is worked until a specific gravity of about ·970 at 60° F. is reached. This distillate is run into the crude solvent naphtha tank. If, however, it is desired to collect two fractions, which is a better plan, then the end of the first is determined when the specific gravity at the worm end reaches about ·930 at 60° F., and the end of the second when a test of the distillate collected as it runs from the coil shows ·980 at 60° F. The former is run to the crude solvent and the latter to the crude heavy naphtha receiver.

The residue in all cases is run to creosote, or else reserved for the recovery of naphthalene. If it is desired to carry out the distillation just described in a steam-heated still, open steam is introduced with care shortly after the distillate appears, unless high-pressure steam is used, and the supply continued until the end of the operation, closed steam, of course, being employed throughout the entire distillation.

The light creosotes from some tars are not rich enough in light oils to call for treatment for the recovery of these, but in some cases it is found that sufficient of the benzene homologues may exist in the creosote to warrant a distillation for the purpose of recovering a fraction from which these materials may be obtained. When this is the case the light creosote is submitted to a distillation in a fire-heated still provided with a fractionating column, and a fraction collected the amount of which will vary considerably, and the finishing point of which will have to be determined by the chemist on the works. After washing this fraction free from tar acids, it is necessary to submit it to a further distillation in a fire-heated still, separating into one or two fractions as is found advisable. The first fraction may be run to the crude solvent and the second to the crude heavy solvent received.

The following Tables 60 and 61, due to Whitehead,[1] are very useful to show the average constitution of crude benzoles as received from gasworks in all parts of Great Britain, using all classes of coal.

TABLE 60

Retorts employed.	Horizontal.		Inclined.	Vertical.
	Steam.	Direct Fire.	Steam.	Steam.
Specific gravity at 15·5° C. . .	0·896	0·899	0·875	0·873
Carbon disulphide	0·5	0·3	0·3	0·3
Paraffins	1·3	1·1	5·3	10·4
Benzene	50·3	39·9	32·2	22·0
Toluene	16·4	18·4	17·8	9·5
Xylenes	8·0	10·2	13·6	16·7
Loss on alkali washing . . .	0·5	0·7	1·0	0·9
Loss on acid washing . . .	5·3	5·5	11·4	8·2
Residue at 170° C. in washed distillate	2·9	3·7	6·9	6·9
Residue at 170° C. in original sample .	14·8	20·2	11·5	25·1

TABLE 61

Crude Benzole from "Steamed" Continuous Vertical Retorts

Gas works.	A.	B.
Specific gravity . . .	0·853	0·856
Paraffins	15·9	12·6
Benzene	15·0	30·8
Toluene	11·2	11·6
Xylenes	25·8	15·1
Loss on acid washing . .	10·6	8·9

The crude benzole crude solvent, and crude heavy naphtha must be submitted to a washing process to remove pyridine bases and impurities. The former substances are of value to the tar distiller, and in almost every case are recovered and refined. Before commencing a wash it is advisable to examine the oil, whichever quality it may be, for tar acids, and if any exist they must be washed out. In all cases, before washing, it is advisable to allow the oils to rest for a time to settle out entangled water. Pyridine is the first member of a series of organic substances which correspond to the general formula $C_nH_{2n-5}N$, and it is represented by the chemical formula C_5H_5N. It possesses basic properties and combines easily with mineral acids, according to the following equations :—

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[1] *Benzole, its Recovery, Rectification and Uses*, Benn Bros., Ltd., London.

$$(a)\ C_5H_5N + HCl = C_5H_5NHCl$$

$$\text{or}\quad (b)\ 2C_5H_5N + H_2SO_4 = (C_5H_5N)_2H_2SO_4$$

A fuller description of the properties of pyridine and its chief homologues will be found in Chapter XVI.

Sulphuric acid is used in all cases to remove the pyridine bases, and the quality usually employed is ordinary B.O.V., of about 146° Tw. In one part of the operation it is used as supplied, and in another part it is diluted. After the pyridine bases are removed, a stronger acid known as D.O.V., of a specific gravity of approximately 167° Tw., is employed. It is then necessary to wash the oils with water, then with caustic soda lye, and finally again with water.

In all cases two washers should be employed, one in which to conduct the acid-washes and the other the caustic soda and the final water-washes. If the acid and soda-washes are conducted in one washer, there is a great risk of some of the resinous matter, produced by the action of the acid, adhering to the sides of the washer, and suffering decomposition by the caustic soda and then being dissolved by the oil. Distillates from the rectifying still off oils to which this has happened will possess a peculiar unpleasant odour and will rapidly go off colour.

Dealing first with crude benzole, one method of washing this material is as follows : A quantity of B.O.V. at 146° Tw., amounting to between 1½ to 2 per cent. of the volume of the oil, is slowly added to the charge of oil in the washer, while it is under vigorous agitation. The period of agitation may be between twenty minutes to half an hour. After this time has elapsed the contents of the washer are allowed to rest for about half an hour, and the greater part of the substance which settles out, known as pyridine acid, is run off into the pyridine acid tank. After a further settling of about half an hour, any more pyridine acid which has separated should be run off, and then about ½ to 1 per cent. of D.O.V. slowly added to the oil, with agitation. The time occupied in agitating in this case may vary from twenty minutes to three-quarters of an hour, but care must be taken that the oil does not become too hot. After the agitation it is allowed to settle for about ten minutes, and as much of the substance (known as acid tar) as has separated removed. The resinification of hydrocarbons brought about by the action of D.O.V. is sometimes considerable, and the acid tar formed often very rapidly solidifies to a " livery " mass, which will not flow, and which has a tendency to adhere to the bottom and sides of the washer. It is policy, therefore, not to lose any time, but to remove as much as possible before this state sets up. Further settlings of ten minutes are given, and any more acid tar which separates is run off. When the whole of the acid tar has been removed—it should be noted that this material must not be run to the pyridine acid tank—the sides of the washer should be carefully washed down with a spray of cold or warm water. This will settle to the bottom, and is removed via the catch tank—in which is separated and retained any oil which may escape from the washer—to a neutralising tank, and from the tank to the drains. After this preliminary wash, the oil is washed with water until the washings are practically free from acid. It is a good plan not to agitate the oil with water when giving the first wash, but to spray water on to the surface of the oil and let it fall through it to the bottom of the washer. When the washing is completed, the oil is pumped, or run by force of gravity, into the second washer and treated with about $\frac{1}{4}$ to $\frac{3}{4}$ per cent. of caustic soda lye standing at 40° Tw. or thereabouts. The soda lye is allowed to separate out, and then run off, and after this the oil is washed with clean water until the wash waters react neutral to litmus. After a thorough settling, the washed oil may be run direct into the rectification still, or to a storage tank, to await treatment at a later date.

With poor classes of crude benzole it is generally necessary to wash with a further 1 to $1\frac{1}{2}$ per cent. of B.O.V. of about 146° Tw., before proceeding with the D.O.V. wash. Whatever the amount of acid used it is not wise to proceed to the water and caustic soda washes until it has been established with certainty that sufficient acid has been employed. A ready method of doing this is to place 90 c.c. of the oil in a stoppered test mixer, add 10 c.c. of pure sulphuric acid, and well shake for five minutes. The mixture is then allowed to stand to separate the acid, which should not be darker in colour than that of a $\frac{N}{10}$ potassium dichromate solution.

It is sometimes found advisable, in fact in the author's opinion it is wise, always to wash the crude benzole with a little dilute B.O.V. before adding the D.O.V. This will ensure a complete removal of the pyridine bases. This dilute acid may be prepared by adding one part of B.O.V. to one part of water, and the amount added to the benzole may vary between $\frac{3}{4}$ and 1 per cent. The total loss of crude benzole by washing varies considerably according to the quality of the oil; however, a good average may be taken as 3 per cent. Some of the crude benzoles contain comparatively large quantities of unsaturated paraffin hydrocarbons, and these, of course, are acted upon by the sulphuric acid used in the washing, and will naturally increase the amount of loss.

In the preparation of pure benzoles from a crude benzole it is often necessary to remove a substance known as thiophene, and also some of its homologues. Thiophene is represented by the chemical formula C_4H_4S. It has a boiling-point of 84° C., a specific gravity of 1·07, is colourless, and possesses an odour similar to that of benzene. Concentrated sulphuric acid dissolves thiophene, and if the solution is treated with a trace of isatin, a dark blue colour is produced. As thiophene so closely approaches benzene with reference to its boiling-point, it is practically impossible to separate it by distillation. It is, therefore, necessary to remove it by chemical washing, and in one method concentrated sulphuric acid is used. In order to carry out this method economically, it is wise to submit the crude benzole to a washing, as just described, and then carefully fractionate it and afterwards rewash the fraction, which represents the once rectified benzole, several times with small quantities of D.O.V. It is essential, of course, to submit the once rectified benzole—

after it has undergone several strong acid washes—to a test for thiophene in the chemical laboratory. When this test gives a satisfactory result, the material may be washed with water and caustic soda, and finally with water, as previously described.

According to English Patent No. 152,470,[1] thiophenes can be removed from benzole by treating it with 60 to 85 per cent. sulphuric acid at a temperature of between 30° and 90° C., or, alternatively, by passing the vapour of benzole through 73 to 82 per cent. sulphuric acid.

P. K. Dutt and J. D. Hamer[2] suggest that thiophene and its homologues can be removed from benzole and toluole by agitating these substances in the cold with the addition of sufficient chlorine to convert the thiophene or thiotolene into their chloro derivatives. The chlorine may be used as a gas or dissolved in water. As these compounds possess high boiling-points they are readily separated by submitting the benzole or toluole after treatment to a fractional distillation. It is necessary to determine by analysis the requisite quantity of chlorine required to carry out the operation, and these workers state that about 1·5 per cent. of chlorine is sufficient to remove 0·5 per cent. of thiophene or thiotolene. For the removal of thiophene, thiotolene, etc., from once distilled benzole, etc., in cases in which the pure products are required for the manufacture of coal tar colours, this process appears to be a very satisfactory one to use.

With reference to the washing of crude solvent naphtha, the process is essentially the same as that already described for crude benzole. It is necessary, however, to use a rather larger quantity of acid, as there is generally a higher percentage of pyridine bases contained in this material, and in order to produce rectified naphthas of good colour. So that the finished products shall be perfectly free from pyridine and able to pass the Weber test for that substance, it is advisable to use some dilute acid, prior to adding the strong acid (D.O.V.) used in the final acid wash. The following is a good method of washing a crude solvent. For the first wash add about 1 per cent. of B.O.V. at 146° Tw. and agitate vigorously for between twenty minutes and half an hour. After the period of agitation, allow to settle to precipitate the pyridine acid, which is run off to the storage tank for further treatment. The second wash of about $1\frac{1}{2}$ per cent. of B.O.V. is now given, the time of agitation being about the same. After the removal of the pyridine acid, the naphtha is submitted to a third wash with dilute B.O.V. This dilute B.O.V. may be prepared by taking one part of acid and one part of water, and the amount used should be about $1\frac{1}{2}$ per cent. Thorough agitation is necessary, and the time should not be less than half an hour. This weak acid wash will completely remove all the pyridine. The contents of the washer should be allowed to settle, and the weak pyridine acid which precipitates run off to the pyridine acid storage tank. At this point it is advisable to submit a sample of the naphtha in the washer to the Weber test (see Chapter XXII, page 430). If it passes this test, a fourth wash with D.O.V. is given. The quantity of this acid, as a rule, need not exceed more than between $\frac{3}{4}$ and 1 per cent. It is sometimes necessary, however, to use rather more, but circumstances will have to decide this. The time occupied in agitating should not be prolonged: usually about twenty-five minutes is ample. After this the contents of the washer should be allowed to rest, to deposit acid tar, and it is just as well to run this material off at intervals of about ten minutes. If it is allowed to remain too long in the washer, there is a risk of its becoming so thick that it will not run through the outlet. The acid tar should not be run to the pyridine acid storage tank, but to a separate receptacle. After the final wash with D.O.V. the acid test should be applied as described on page 271.

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[1] South Metropolitan Gas Co., E. V. Evans and H. Hollings, Eng. Pat. 152,470. August 16th, 1919.

[2] Eng. Pat. 117,683, July 27th, 1917.

At least 1½ hours should be allowed for settling before the water washing is commenced, and it is advisable to thoroughly wash down the sides of the washer, and also spray the water on the surface of the naphtha, allowing it to fall through it by force of gravity, before any water is agitated with the oil; the water which separates during this process is removed before agitation with clean water is commenced. Further water washes are now given with agitation, which must not be too vigorous. When the wash water comes away from the naphtha practically neutral, a short time for settling is allowed, and the drainings removed. The naphtha is then pumped, or allowed to run by force of gravity, into a second washer for treatment with caustic soda lye of about 35°–40° Tw. A large amount is not necessary, the quantity usually varying between ¼ to ½ per cent. After about twenty minutes' agitation, the contents of the water should be allowed to settle thoroughly, the lye wash removed, and the naphtha then submitted to water washes as already described. It is necessary that clean water be used and the last wash water should come away from the naphtha quite neutral to litmus. When this is the case, the washed crude solvent may be removed to a storage tank or direct to the rectification still.

Many of the crude solvents when washed with strong acid deposit an excess of acid tar, often of a very resinous nature. A good method of avoiding this is to submit the crude naphtha to a second distillation before washing with acid, *i.e.* distilling the crude solvent in a steam-heated still, and collecting practically the whole of it in one fraction. This fraction, when washed in a similar fashion to that just described, appears to give very little acid tar in the final acid wash. There is also a great improvement as regards the odour of the rectified material. The total loss of crude solvent varies to a much greater extent than that of crude benzole; it may be between 5 and 13 per cent.

In washing crude heavy solvent, a good deal of discretion is necessary. This class of material will contain varying quantities of naphthalene, and in the washing, especially with D.O.V., some of this material becomes sulphonated and is lost; in fact, if not carefully conducted, the loss may amount to as much as 25 per cent. It is generally necessary to use some D.O.V. if a rectified heavy naphtha which will keep its colour when exposed to the light is desired. The method of washing is exactly the same as has already been described, and the average amount of B.O.V. used at 146° Tw. is 2¼ per cent.; of dilute B.O.V. (1 : 1) ½ per cent.; and of D.O.V. 1½ per cent. It is advisable to divide the quantity of B.O.V. so that three washes may be given with it, and with the D.O.V. two. A wash with caustic soda lye of about 35°–40° Tw. must not be forgotten, the amount used being between $\frac{1}{2}$ and $\frac{3}{4}$ per cent., calculated on the volume of the crude heavy solvent. Water washes must be thorough, and it is absolutely necessary to secure neutrality after the acid and soda washes.

R. Kattwinkel[1] suggests that if boric acid is added to the sulphuric acid used for washing crude benzole, the resinous matter formed is reduced by about 25 per cent., and the increase in the yield of benzole averages about 2 per cent. He states that the action of the boric acid appears to be due to the formation of a compound with the phenolic constituents.

This worker apparently is not aware of the fact that in well-managed benzole distilleries all the phenolic bodies are removed from crude benzole before washing it with acid.

The treatment of benzole acid sludge or acid tar has received the attention of tar distillers from time to time, and subjecting this material to distillation has often been tried by one worker or another. Stephenson[2] found that a tall, narrow still is unsuitable for the recovery of benzole from acid tar owing to the fact that frothing occurs, and he came to the conclusion that the steam to be used for distillation should be introduced through a number of orifices. He therefore designed a still on these lines and provided for a jet of ammonia gas to be introduced into the swan neck in order to neutralise the sulphur dioxide given off during the process. By the use of this still benzole suitable for the market was produced. From a charge of acid tar 20 per cent. of benzole was recovered. The residual acid liquor from various charges was found to be of a strength between 33 and 55 per cent. calculated as sulphuric acid. A black resinous residue which contains approximately 1 per cent. of ash is also obtained, and this material is found to be suitable as a fuel; or if washed with water, dried and then distilled, it will yield approximately 15 per cent. of oil. In the acid liquor mentioned above, pyridine bases were found in amounts up to 8 per cent.

Resins suitable for the manufacture of various types of varnish can now be prepared from solvent naphthas or heavy benzoles by an acid polymerisation of the cumerone, indene and similar hydrocarbons present in these oils.[3] It has been found that greater uniformity of resin product will be obtained if crude naphthas of varied composition are mixed, the amount of each quality of naphtha being determined so as to obtain a product yielding about 30 per cent. of resin. It is possible to obtain a light-coloured resin by subjecting naphtha with or without an initial blending, and after the removal of the tar acids and pyridine which it contains, to a preliminary polymerisation by means of sulphuric acid of a strength of 60° to 66° Bé, using about 0·1 to 0·5 per cent. and removing the dark-coloured constituents formed. The oil is then subjected to a neutralising process and afterwards distilled, and then subjected to the main polymerisation, which is effected by using 1 to 3 per cent. of sulphuric acid of about 62° Bé. The spent acid and tar are removed from the resin-containing oil, the oil is then neutralised with alkali, washed with water and distilled *in vacuo*. A final distillation *in vacuo* with the introduction of superheated steam is carried out in order to remove naphthalene and heavy oils and leave the molten resin at the bottom of the still, from which it is drawn off.

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[1] *Brennstoff-Chem.*, 1922, 3, 357–360.

[2] *Gas World*, February 5th, 1921, Coking Section, 19–21.

[3] Eng. Pat. 142,806, Barrett Co. New York, U.S.A.

Crude benzole contains, among other impurities, a fair amount of carbon disulphide, and this objectionable substance is, in practice, removed in the process of rectification, as will be mentioned in the next chapter. J. A. Wilson, English patent 14,152, 6th October, 1915, claims that benzene can be freed from carbon disulphide, before or after rectification or treatment with sulphuric acid, by agitating with caustic soda (20°–25° Tw.) at a temperature below the boiling-point of the benzene.

In a method suggested by J. E. Thompson[1] for purifying crude benzole from carbon disulphide, the benzole is mixed with aqueous ammonia of about the same, but of not greater specific gravity than the benzole. The impurities which combine with the ammonia are allowed to subside, and the supernatent purified benzole is removed and submitted to distillation or any other desired process.

According to H. G. Colman and E. W. Yeoman[2], carbon disulphide can be readily extracted from benzole or other liquids containing it by agitating the material with a cold, aqueous solution of an alkali or alkaline-earth bisulphide. With these compounds carbon disulphide forms a salt of perthiocarbonic acid, H_2CS_4. The perthiocarbonate, after separation from the benzole, is decomposed by the addition of mineral acid with the production of carbon disulphide, hydrogen sulphide, and sulphur, and these substances are separated by submitting the mixture to steam distillation. The carbon disulphide is condensed, the hydrogen sulphide absorbed in hydrated ferric hydroxide, and the sulphur is recovered by filtering the still bottoms. The sulphur can be used in the preparation of more bisulphide solution. Instead of decomposing the perthiocarbonate, it may be employed as a bactericide. If, instead of decomposing the perthiocarbonate by means of acid, soluble iron salts or ferric hydroxide be employed, a precipitate of ferrous sulphide and sulphur is obtained, which, on exposure to the atmosphere, oxidises to ferric oxide and sulphur. On submitting the perthiocarbonate solution to simple distillation a distillate of carbon disulphide and sulphuretted hydrogen are obtained, and a residue of polysulphide and hydroxide remains. This residue can be converted into alkali bisulphide again. The escaping non-condensable gases which contain some carbon disulphide may be purified of sulphuretted hydrogen by treatment with lime and hydrated ferric oxide, and the carbon disulphide recovered as cellulose xanthate by a subsequent passage through an alkali-cellulose solution.

An interesting process for the purification of benzole has been recently described.[3] The crude benzole is purified by first vaporising it by known means and then passing it through sulphuric acid and a caustic alkali solution successively, and then (after any further desired treatment) condensing the purified vapour by known or any convenient means. For this purpose an apparatus (see Fig. 105 for a diagrammatic illustration) is provided which consists of a still R, a dephlegmator S, and analyser T, all of known or convenient construction, a compartment for sulphuric acid D, a compartment for aqueous caustic alkali solution E, and a condenser U. By this method and means the purification process may, if desired, be made continuous, and the purification is carried out in a single process.

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[1] U.S. Pat. 1,276,284. August 20th, 1918.

[2] Eng. Pat. 145,099. December 20th, 1918.

[3] Eng. Pat. 10,066 of 1915. Gerald L. Moss and Simon-Carves' By-Product Coke Oven Construction and Working Company, Limited, 20 Mount Street, Manchester. Date of application, July 10th, 1915.

The compartments D and E are surrounded by a steam-jacket, by which this vessel is maintained at a temperature not less than that at which the benzole vapour enters, to avoid condensation of the vapour when within the vessel. The benzole first bubbles through the sulphuric acid, then goes down the passage B, and bubbles up through the alkali solution. Baffles are provided in the compartments D and E to arrest any liquid spray that may be carried by the benzole vapour.

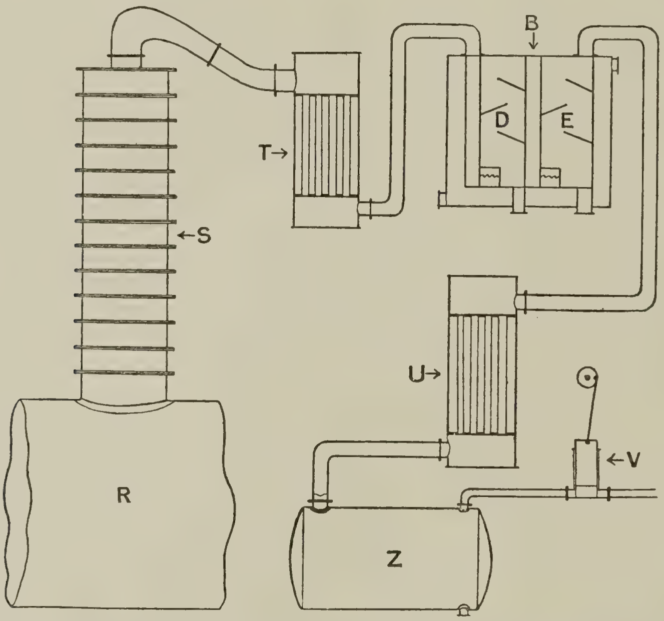

Fig. 105.—Moss and Simon-Carves' Apparatus for Benzole Purification.

The concentration of the acid solution is preferably 168° Tw. to commence with, and should be maintained as near as possible thereat if the best results are to be obtained. Good results can, however, still be obtained with a concentration of 160° Tw. Care should be taken that the caustic alkali solution is not or does not become of too high a concentration, as, owing to the rapid evaporation of the water, sulphate crystals are liable in that case to be formed and thus obstruct the clear working of the apparatus. A suitable concentration is 30° to 40° Tw.

The pump V maintains a vacuum throughout the whole circuit, and the purified benzole is collected in Z.

Although the process is described as being carried out with the aid of an ordinary intermittent still, it will be understood that it may be applied equally to a continuous still, and in that case a complete unit may be provided for each fraction.

An ingenious method for removing sulphur from oils by the aid of a catalytic agent, and which is applicable to the purification of benzoles and naphthas, has been invented by E. V. Evans, of the South Metropolitan Gas Company.[1] The following is a brief description of it :—

The sulphur is eliminated as sulphuretted hydrogen by heating the oil in presence of hydrogen or gas containing free hydrogen and a catalytic agent or contact substance. In the case of an oil of suitable boiling-point, the vapour of the oil mixed with a small proportion of hydrogen (5 or 10 per cent. of its volume) may be passed over the heated catalytic or contact substance and the sulphuretted hydrogen removed from the vapour by absorption by any known agent, or the oil may be washed after condensation to the liquid form.

The most efficient temperature of working is in the region of 400° to 500° C., for at this temperature the iron pipes which contain the catalyst or contact substance are not destroyed, and the velocity of the reaction is so high that a relatively small area of contact is required. Certain oils are, however, decomposed at these temperatures, and when this is to be avoided lower temperatures must be employed. To this end a relatively greater surface of contact will be necessary in order to bring about a similar effect as at 400° to 500° C. It is necessary, therefore, to determine with each particular oil the maximum temperature, below 500° C., at which the oil is not decomposed, and to allow sufficient contact with the catalytic or contact substance to ensure that practically the whole of the sulphur of the oil is converted into sulphuretted hydrogen.

The distillation of naphtha from crude coal tar is cited as an example of the application of the process. The vapours from the still are conducted to a furnace maintained at 450° C., in which steel or iron pipes are contained. A convenient arrangement for these pipes is in the form of a U. The vapours enter at the top of one limb and in descending are brought to the temperature of the reaction. To enhance this, the limb may be packed with non-combustible material. The catalytic material is placed in the second limb. Assuming that the rate of distillation is 50 gallons per hour, the volume of each limb of the U-tube should be about 7·5 cubic feet. A stream of hydrogen or coal gas is introduced at the inlet of the preheating tube or tubes and allowed to flow with the vapours at the rate of about 400 to 500 cubic feet per hour. Only a small portion of this hydrogen is actually used, and it is advisable to pump the hydrogen over in a closed circuit. The sulphuretted hydrogen produced as a result of the decomposition of carbon disulphide and sulphur compounds is washed from the condensed vapour by caustic soda solution, or it may be extracted direct from the vapour by means of an oxide of iron purifier kept sufficiently warm to prevent condensation.

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[1] Eng. Pat. 22,147 of 1914. Edward V. Evans and the South Metropolitan Gas Company, 709 Old Kent Road, London. Date of application, November 6th, 1914.

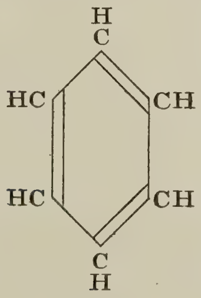
In the case of an oil which cannot be distilled the catalytic substance may be introduced into the liquid oil, which is suitably heated while hydrogen is passed through it, or the heated oil may trickle over the catalytic substance while hydrogen is at the same time passing over it.

CHAPTER XIV

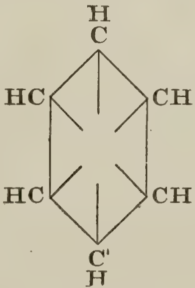
RECTIFICATION OF BENZOLES AND NAPHTHAS

THE composition of crude benzole and also of crude solvent naphtha varies somewhat according to the quality and kind of tar from which they are recovered, but benzene, toluene, and the three xylenes occur in one or other of them in considerable quantity, and a brief description of the chemical and physical properties of these substances will not be out of place in this chapter.

Benzene (C_6H_6) is a colourless, highly refractive, mobile liquid possessing a peculiar but not unpleasant smell. Its specific gravity at 0° C. is 0·899; at 15° C., 0·882; at 20° C., 0·8791, and at 25° C., 0·876. When cooled in a freezing mixture it solidifies to a mass of colourless orthorhombic prisms which melt at 5·4° C. (corr.). The melting-point of benzene is affected by an increase in pressure or by saturating it with water. The freezing-point of benzene free from air is increased 0·029° C. per atmosphere, whilst saturation with water lowers the freezing-point 0·095° C.[1] Its refractive index at 20° C. is 1·4967, and its molecular volume at the same temperature is 88·65. Benzene boils at 80·36° C. (corr.). At ordinary temperatures 100 c.c. of water will dissolve approximately 0·01 c.c. of benzene. According to Kopp, its specific heat between 19° and 46° C. is 0·450. It is soluble in alcohol, ether, acetone, etc., and is an excellent solvent for resins, fats, ethereal oils, and many other organic compounds. Sulphur, iodine, and phosphorus are also soluble in benzene. With reference to the constitutional formula of benzene several have been suggested, but those of Kekulé and Armstrong have received the most support.



Kekulé.



Armstrong.

An important contribution dealing with the constitution of benzene is published by Ronald Fraser.[1] This worker attempts to apply the newer and more powerful stereochemical methods to the problem of the constitution of this substance, and the paper is worth serious consideration by the earnest student.

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[1] T. W. Richards, E. K. Carver and W. C. Schumb, *Jour. Amer. Chem. Soc.*, 1919, 41, 2019–2028.

To those readers interested in the structure of the benzene nucleus, the writer recommends the perusal of two papers by Christopher Kelk Ingold,[2] one of which deals with intra-nuclear tautomerism, and the other with the synthetic forms of the bridged modification of the nucleus.

A very striking theory on the constitution of benzene is published by Nat. H. Freeman[3], which the reader may care to peruse. Following this paper there was a considerable amount of discussion. The foot-notes give the name of the Journal and the dates on which the article and discussion appeared.

Benzene forms additive compounds with some unsaturated hydrocarbons, *e.g.* styrene with benzene forms diphenylethane,

$$C_6H_5CH:CH_2+C_6H_6=(C_6H_5)_2CH{\cdot}CH_3.$$

Diphenylpropionic acid is formed if benzene is allowed to act upon cynamic acid in the presence of sulphuric acid,

$$C_6H_5CH:CH{\cdot}COOH+C_6H_6=(C_6H_5)_2CH{\cdot}CH_2{\cdot}COOH.$$

The vapour of benzene at a low pressure will absorb the Tesla radiations and become feebly luminescent. This effect may be intensified in various ways: (1) by the introduction of an auxochrome (an amino or hydroxyl group); (2) by the multiplication of aromatic nuclei, especially condensed nuclei, such as naphthalene, anthracene, etc.; (3) by the linking of nuclei with unsaturated carbon chains, such as stilbene, $C_6H_5{\cdot}CH:CH{\cdot}C_6H_5$ and diphenylbutadiene $C_6H_5{\cdot}CH:CH{\cdot}CH:CH{\cdot}C_6H_5$.

Benzene is optically coloured, for it produces a banded spectrum in the ultra-violet.

Benzene is a very stable substance, resisting the action of all the mild oxidising agents, and even when boiled with solutions of powerful oxidising agents, such as potassium permanganate or chromic acid, it is only very slowly acted upon. Dilute nitric acid has no action upon it, but strong nitric acid, especially in the presence of concentrated sulphuric acid, attacks it, forming nitro-compounds.

$$1.\ C_6H_6+HNO_3=C_6H_5{\cdot}NO_2+H_2O.$$
$$2.\ C_6H_6+2HNO_3=C_6H_4{\cdot}(NO_2)_2+2H_2O.$$

Concentrated sulphuric acid acts upon benzene very slowly at ordinary temperatures, but at its boiling-point it is acted upon more rapidly, forming benzene sulphonic acid—

$$C_6H_6+H_2SO_4=C_6H_5{\cdot}SO_3H+H_2O.$$

Fuming sulphuric acid converts benzene into benzene disulphonic acid, $C_6H_4{\cdot}(SO_3H)_2$.

Chlorine and bromine act upon benzene in a very peculiar manner. In the presence of direct sunlight, or at fairly high temperatures, additive products are formed, such as hexachlorobenzene, $C_6H_6Cl_6$, and hexabromobenzene, $C_6H_6Br_6$; but in diffused light and at ordinary temperatures benzene is slowly attacked, substitution products being formed, such as chlorobenzene, C_6H_5Cl, dichlorobenzene, $C_6H_4Cl_2$, bromobenzene, C_6H_5Br, etc. Iodine appears to have very little action upon benzene.

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[1] "A Note on the Constitution of Benzene," *J.C.S.*, 1922, No. 711, p. 188, Trans.

[2] *J.C.S.*, 716, June, 1922, pp. 1133–1143 and 1143–1153.

[3] *Chem. Trade Jour.* and *Chem Eng.*, July 10th, 1920, p. 41; July 24th, 1920; August 7th, August 21st, 1920; September 4th, 1920; October 9th, October 23rd, 1920.

It has been shown by J. M. Weiss and C. R. Downs that it is possible to obtain from benzole such organic acids as tartaric, citric, lactic, and succinic. The basis of the process is a method of building up various substances from maleic acid obtained from benzole by mixing the vapour of this substance with air and passing the mixture over a suitable catalytic agent. By this new process the authors believe that an entirely new field of synthetic organic chemistry has been opened up.

If benzene is oxidised[1] by using vanadium dioxide as a catalytic agent, quinone is first formed, and this becomes oxidised to maleic anhydride, and if the oxidation is carried further carbon dioxide and water result. It appears that temperature is the controlling factor in this process of oxidation.

Benzene can be oxidised to maleic acid, $C_4H_4O_4$, in the presence of vanadium oxide as a catalyst.[2]

If a mixture of benzene vapour and hydrogen is passed at a pressure of about 300 lbs. per square inch over a catalyst such as nickel oxide, the temperature being maintained at about 300° C., cyclohexane results. By adjusting the rate of feeding the benzene into the apparatus, hydrogenation may be effected to yield a mixture of cyclohexane and benzene in any desired proportion.[3]

On submitting benzene to electrolytic oxidation, over 80 per cent. of quinone has been obtained by H. Inoue and M. Shikata.[4]

Benzene can also be oxidised to quinone at the anode of an electrolytic cell, and afterwards reduced to quinol.[5]

It is stated that if ozone is led into benzene the latter is oxidised with the formation of acetic acid, formic acid, and also oxalic acid.

According to Harries and Weiss, ozone forms with benzene an explosive compound which is called ozobenzene. By the action of hydrogen peroxide benzene is oxidised into oxalic acid and phenol.

J. Timmermans[6] has obtained from commercial benzole normal heptane and a heptamethylene. The quantity present was not large, being less than $\frac{1}{3000}$ of the weight of the benzole taken.

The following figures dealing with commercial benzole and pure benzene are given by H. J. Pooley :—

	B. Pt. °C.	Specific heat.	Latent heat. Cal/grams.
Commercial Benzole . .	79·12	0·408	95
Pure Benzene . . .	80·3	0·41	93·4

Toluene, methyl benzene, phenyl methane, $C_6H_5{\cdot}CH_3$, is a colourless, highly refractive, mobile liquid, with an odour somewhat similar to that possessed by benzene. At 15° C. its specific gravity is 0·872, at 20° C. 0·866, and at 25° C. 0·8625. It solidifies below—100° C. forming colourless crystals which melt at—93·2 C. (corr.). The boiling-point of toluene is 111° C. (corr.). With regard to solvents and its solvent action it behaves very similar to benzene. It largely resembles benzene in its chemical properties, differing principally in those which are due to the presence of a side chain (the methyl group). The constitutional formula of toluene is written thus—

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[1] J. M. Weiss and C. R. Downs, *Jour. Ind. Eng. Chem.*, 1920, 12, 228–232.

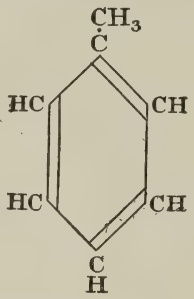
[2] Eng. Pat. 167,219, The Barrett Co.

[3] Eng. Pat. 133,666, May 7th, 1919.

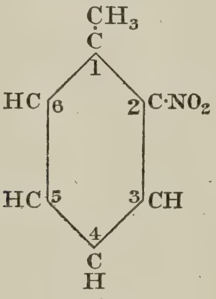
[4] *Jour. Chem. Ind. Japan*, 1921, 24, 567. See also *J.S.C.I.*, 1921, 652A.

[5] U.S. Pat. 1,322,580.

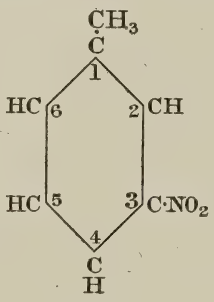
[6] *Bull. Soc. Chem., Belg.*, 1920, 29, 227–229.



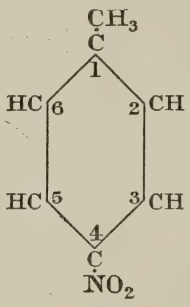
Its behaviour with sulphuric and nitric acids resembles that of benzene in so far as it yields sulphonic and nitro-derivatives. These compounds, however, exist in three isomeric forms, viz. ortho, meta, and para. For example, mono-nitrotoluol exists in three forms represented by the following constitutional formulæ :—



Ortho.

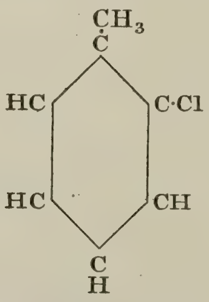


Meta.

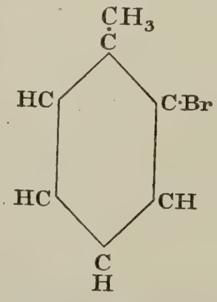


Para.

At ordinary temperatures and in diffused light chlorine and bromine act on toluene, producing substitution products by displacing the hydrogen of the benzene ring or nucleus, thus :—

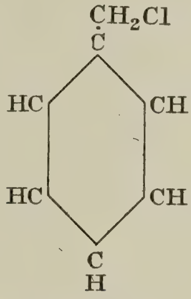


Ortho-chloro-toluene.

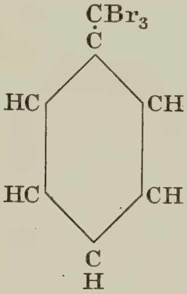


Ortho-bromo-toluene.

If, however, toluene is acted upon by chlorine or bromine at its boiling-point, or in direct sunlight, substitution of hydrogen of the side chain or methyl group takes place, thus :



Benzal chloride.



Benzo-tribromide.

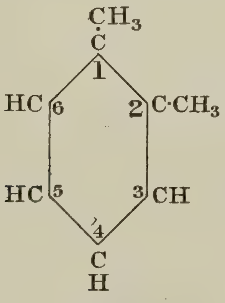
By the strong oxidising agents toluene is converted, with difficulty, into benzoic acid, the methyl-group or side chain being oxidised.

$$\underset{\text{Toluene.}}{2C_6H_5\cdot CH_3}+3O_2=\underset{\text{Benzoic acid.}}{2C_6H_5\cdot COOH}+2H_2O.$$

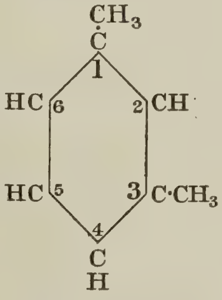
If the vapour of toluene and air are passed over vanadium pentoxide at a temperature of 350° to 450° C., benzaldehyde and some benzoic acid are formed.[1]

Toluene, according to The New Process Gasolene Co.,[2] can be obtained, among other substances, by heating a spruce turpentine with aluminium chloride, and distilling the liquid obtained in the presence of hydrochloric acid.

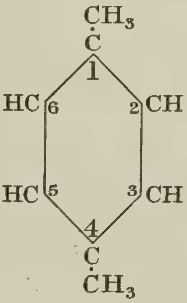
Xlyene, dimethyl benzene, $C_6H_4(CH_3)_2$ exists in three isomeric forms, viz. ortho, meta, and para. The constitutional formulæ of these isomers are :—



Ortho-xylene.



Meta-xylene.



Para-xylene.

Some of its physical properties are given in Table 62 ; and in Table 63, constructed by Professor Richards and Mr. C. L. Speyers, after making many careful observations, will be found some useful constants.

The three isomeric xylenes are colourless liquids possessing aromatic odours dissimilar to those of benzene and toluene. Their behaviour with concentrated sulphuric and concentrated nitric acids is very similar to that of toluene, sulphonic acids and nitro-compounds being formed. In the case of the para isomer it is necessary to use fuming sulphuric acid to obtain the sulphonic acid. Oxidising agents act upon the three isomers with moderate ease forming the toluic and phthalic acids by oxidising, in the former case one and in the latter case both of the methyl groups. Chlorine and bromine act upon the xylenes in a similar manner to the way in which they act upon toluene.

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[1] U.S. Pat. 1,261,022, Greenley.

[2] U.S. Pat 1,244,444, October 23rd, 1917.

According to U.S. Patent No. 1,334,033, if xylole is subjected to the action of anhydrous aluminium chloride, toluene is produced and can be distilled off continuously.[1]

TABLE 62

Isomer.	Specific gravity.		Melting-point, corr.	Boiling-point, corr.	Solubility in		
	At 0° C	At 25° C.			Water.	Alcohol.	Ether.
Ortho	0·8932	0·876	—29° C.	142° C.	Insol.	Sol.	Sol.
Meta	0·8810	0·863	—54° C.	138·5–139·5° C.	Insol.	Sol.	Sol.
Para	0·8801	0·859	15° C.	137–137·5° C.	Insol.	Sol.	Sol.

TABLE 63

Substance tested.	Boiling-point in Deg. C.	Density at 20° C., compared with water at 4° C.	Surface tension at 20° C., in milligrammes per millimetre.	Compressibility at 20° C. × 10^6.
Orthoxylene	144·0	0·8811	3·09	60·0
Metaxylene	139·0	0·8658	2·96	63·5
Paraxylene	136·2	0·8611	2·92	65·2

The chief products obtained by the rectification of crude benzole are 90's benzole and 50–90's benzole, and by a second rectification commercially pure benzole, which will yield about 95 per cent. within $\frac{1}{2}$ to $\frac{3}{4}$ of a degree C. Crude solvent naphtha on rectification will yield a large number of products, many of which are specially made to the specification of buyers. There are several grades of solvent naphtha, the chief of which is known as 90 per cent. at 160° C. Some of the other grades obtained are solvent naphtha yielding 95 per cent. at 165° C. or 90 per cent. at 190° C., and also those possessing flash-points of 75° and 85° F. (Abel's close test). Commercial toluole is also obtained from crude solvent naphtha, and, by a second rectification, commercially pure toluole and commercially pure xylole. Crude heavy naphtha will yield various grades of heavy naphtha, the quality, specific gravity, flash-point, and distillation of which will vary according to the requirements of the buyer.

It is not possible to give here full particulars as to how all the products that may be obtained from these materials are prepared, but brief consideration will be given to the method of producing some of the chief products.

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[1] E. I. du Pont de Memours and Co., Wilmington, Del.

Dealing with crude benzole with the object of making 90's benzole, a charge of washed crude benzole is run into the rectifying still and closed steam turned on. When the contents of the still become heated throughout, the steam is slackened a little and the worm end carefully watched. As soon as liquid appears at the worm end, the steam should be regulated to a degree which will allow of the distillate running continuously, and not too fast. The material which comes over first from the washed crude benzole is termed " fronts," and contains a considerable quantity of carbon disulphide (CS_2) and also some low-boiling paraffins. This must not under any circumstances be mixed with the 90's benzole fraction which follows the " fronts," but allowed to run into a separate receiver for further treatment. The carbon disulphide can be removed by chemical means (see Chapter XIII, page 275), and if this is done, then the quantity of " fore-runnings " will not be so great and the quality will be enhanced. When the distillate at the worm end reaches a specific gravity of ·890 to ·898 at 60° F., or shows a drop point of about 70° C. when tested in a retort, the tap on the " fore-runnings " or " fronts " main is closed, and that on the 90's benzole main opened, in order that the condensate may run into the 90's benzole tank. Distillation is now proceeded with until a sample collected from the worm end, and submitted to a test in the chemical laboratory, does not begin to distil until 100° C. is reached. If " standard benzole " is required the drop-point should be about 88° C. It is, of course, necessary to make tests in the laboratory from time to time in order to guide the stillman. When the point just mentioned is reached, the flow of the distillate is cut off from the benzole tank and allowed to run into another receiver for working up with washed once distilled or crude solvent naphtha. In some works the 90 per cent. at 160° solvent naphtha fraction from washed crude solvent is run into this receiver. From the " cutting " point 100° C. [or 88° C.], distillate is collected until a test from the worm end does not commence to boil until 130° C. is reached, when the distillation is generally stopped, and the residue either run to a storage tank to await treatment with further bottoms, or on to it is charged some washed crude solvent. Instead of finishing at 130° C. a 90's toluole fraction can be obtained after the 90's benzole, see page 287.

If it is desired to produce 50's–90's benzole, then the 90's benzole fraction is cut a little earlier (about the point when a sample from the worm end on testing shows no distillate until a temperature of 95° C. is reached) and a fraction collected from this point until one is reached at which the distillate, when tested in the laboratory, does not commence to boil until about 120° C. is reached. This fraction is run to a special 50's–90's tank, to be dealt with later. Sometimes this quality of benzole is made by adding to the fraction collected some lighter material. At times, however, the fraction itself will yield benzole answering to the tests required, *i.e.* 50 per cent. at 100° C. and 90 per cent. at 120° C. The residue in the still is removed to a storage tank to await treatment with other bottoms, or else washed crude solvent is charged on to it.

With reference to the methods of making 90 per cent. toluole and also commercially pure benzene, toluene, and xylene, a brief description is given a little further on.

The washed crude solvent is charged into an empty rectification still, or else on to the residue from a distillation of crude benzole. Distillation is commenced by the use of closed steam, and the first fraction is collected until a sample taken from the worm end and tested in the laboratory begins to boil at about 100° C. This fraction is generally run into the crude benzole storage tank for working up with another batch. For some classes of benzole, however, this fraction may be run into the 90's benzole receiver. It is necessary to introduce open steam shortly after the distillation commences, but it is not advisable to do this until absolutely essential, and when it is the steam must not be turned on too rapidly. If it is desired to make 90 per cent. at 160° C. solvent naphtha, the end of the next fraction is determined when a sample tested at the worm end shows a specific gravity of about ·895 at 60° F., or, if submitted to a distillation test in the laboratory, does not begin to boil until 160° C. is reached. It is advisable when working for this, and even other qualities of naphtha, to occasionally test the material in the receiver after a thorough stirring up. For instance, in the case of solvent naphtha, to find what percentage is given off at 160° C. ; in fact, some stillmen prefer to have their tank tested for the percentage of distillate yielded at 160° C., as the collection of this fraction comes to a close, rather than making tests at the worm end. It is necessary, of course, to discontinue running the distillate into the solvent naphtha tank as soon as the contents of that tank yield 90 per cent. at 160° C. when tested in a retort.

If it is desired to produce a solvent naphtha possessing a distilling range between 135° and 160° C., then a "toluole-xylole" fraction must be removed before running the distillate into the solvent tank. This fraction is run between the points at which the distillate from the worm end gives a drop test of 100° and 130° C. The special solvent naphtha fraction is then collected and discontinued when the drop test of the distillate from the worm end shows 160° C.

After the solvent naphtha fraction has finished coming over, the distillate is turned into another receiver. This fraction yields what is known as heavy naphtha, and the quality of this naphtha will vary according to how far the distillation is carried, or whether one or more fractions are collected. If it is desired to make a very heavy naphtha, giving about 60 per cent. at 190° C., then the distillation is finished when a sample at the worm end shows a specific gravity of ·980 to ·990 at 60° F. Other qualities of heavy naphthas may be prepared by stopping the collection of the distillate at an earlier point. The residue left in the still is either run to creosote or else to a special tank, to be worked for naphthalene.

If it is desired to manufacture from the crude solvent fraction a naphtha possessing a flash-point of 75° F. (Abel's closed test), and giving 90 per cent. at 160° C., then the following method is adopted. The distillation is commenced and the lighter portion is turned into the crude benzole tank, as already described, and then a further fraction is collected until a test of the material taken from the worm end shows no distillate until 132° to 134° C. is reached. This fraction is run into a special tank for re-distillation, or into the solvent naphtha tank, according to conditions obtaining in the works. The distillation is continued from this point until a sample collected from the worm end does not begin to distil until about 160° C. is reached. This fraction will give a 75° flash naphtha with a distillation test as already mentioned. The remaining material in the still may be worked for heavy naphthas.

Should it be required to manufacture a solvent naphtha yielding 90 per cent. at 165° C. and possessing a flash-point of 85° F., then the crude solvent is worked first of all for the lighter fraction, as mentioned above, and then a second fraction is taken off, the end of which is determined when the distillate at the worm end, on testing in the laboratory, does not begin to distil until between 138° and 140° C. Between this point and that at which the distillate at the worm end when tested yields 45 per cent. at 165° C. the desired fraction is obtained. The residue in the still is worked for heavy naphthas as previously described.

In making these two qualities of solvent naphtha, a great deal will depend upon the rate of distillation, construction of fractionating column, etc. The slower the rate of distillation the larger the quantity of special material obtained from the charge. It is a very good plan to collect the fraction in, say, 50 or 80-gallon drums, as this will avoid the risk of spoiling the whole. A sample may be taken from each drum, bulked and tested, and then, if necessary, the contents of certain drums may be cut out before bulking.

Commercial toluole yielding 90 per cent. at 120° C. is obtained as a rule from crude benzole. This fraction is collected between the point at which a sample of the distillate, when tested, yields nothing until 100° C. is reached, and a further sample when tested does not commence to distil until 118° C. is attained. This point will vary a little according to the quality of the crude benzole.

In the manufacture of commercially pure benzene, toluene, and xylene, the method of procedure has to be varied somewhat, it being necessary first of all to distil the crude benzole into three fractions, and then to re-distil these fractions. In the first distillation the crude benzole is separated into a "fronts" fraction in the manner already described, and then a first fraction is collected until a test of the distillate leaving at the worm end yields nothing until 95° C. is reached. The second fraction is collected between this point and that at which a sample of the distillate collected from the worm end and tested does not begin to distil until 120° C. is reached. A third fraction is now collected between the "change over" points just mentioned (120° C.) and when the condensate at the worm end commences to distil at 155° C. This fraction is used for the manufacture of commercially pure xylene. The residue is run to a storage tank to be worked up at another time with solvent naphthas.

The first fraction is submitted to a further distillation in a still provided with a dephlegmator. It should be added here that if desired the crude benzole need not be washed before the first distillation, but the washing be carried out on this fraction and the second fraction obtained in the manner already mentioned. In washing like this, less resinous material is obtained and generally a better quality of product is secured. During the distillation of the first fraction for commercially pure benzene, it is necessary to keep the water in the dephlegmator at a temperature of about 45° C. It is essential to separate a little "fore-runnings," working the still slowly during this process and "changing over" when a sample collected at the worm end and tested does not commence to boil until 80° C. is reached. The process is continued and the distillate, and also the contents of the receiver, are tested throughout the operation in order to keep the fraction as close as possible to the desired distilling range, viz. one which will yield 95 per cent. within about three-quarters of a degree. The finishing-point is generally determined when a sample of the distillate collected as it leaves the worm end and tested does not yield a drop until 81·5° C. is reached. Another quality of commercially pure benzene which drops at 79·5° C. and distils all over under 1° is prepared by collecting a fraction between the points at which a sample collected at the worm end and tested drops at 79° C. and another sample which when tested drops at about 80·5° C. Some manufacturers prefer to collect the distillate in 50- or 80-gallon drums, and then test the drums and make a suitable mixing. This is a very satisfactory method. Commercially pure benzene should commence to boil at 80·5° C. and yield 95 per cent. at about 81·3° C.

The second fraction obtained from the crude benzole is worked up together with any residue from the first fraction for commercially pure toluene. This charge is worked comparatively slowly until a sample collected at the worm end and submitted to a distillation shows an initial drop at about 109·5° C. At this point the distillate is "changed over" and the fraction just obtained may be worked up with other material for commercially pure benzene. During the working off of this fraction the water in the dephlegmator should be kept at about 45° C. From the "change over" point just mentioned, distillation is allowed to proceed at a somewhat faster rate, but careful control of the steam supply to the still must not be relaxed. Distillation is carried on until a sample collected at the worm end and tested does not begin to boil until a temperature of 110·5° C. is reached, when the operation is discontinued and the bottoms used for the manufacture of commercially pure xylene. During the working off of the toluene fraction the water in the dephlegmator is kept at about 100° C. Another method of working for the commercially pure toluene fraction is to commence collecting when a sample taken from the worm end and tested commences to distil at 109° C. (or 110° or 111° C.), and then work the still very carefully until the distillate as it leaves the worm end ceases to yield 95 per cent. within 0·8 of a degree from the chosen collecting point. The distillate may be collected into one tank and frequently tested during the operation, or else in drums which are dealt with as described under commercially pure benzole. Commercially pure toluene may also be manufactured from 90 per cent. toluole by a similar method to that just described. It should commence to boil at 111° C. and yield 95 per cent. at about 111·8° C. Some buyers demand a grade which drops at 109° C. and yields 95 per cent. at 110° C., others one which drops at 109·8° C. and yields 95 per cent. at 110·8° C.

Commercially pure xylene is obtained from the residue left from the distillation of pure toluene and from the third fraction from crude benzole (see page 287). This mixture is worked up in a still provided with a dephlegmator, but almost all the water in the dephlegmator is removed so that the remainder will be converted into steam. The fraction collected for pure xylene comes over between the point at which a sample collected at the worm end and tested in the laboratory does not distil until a temperature of about 136·5° C. is reached, and that at which a further sample when tested shows no distillate below about 139° C. These points will vary a little according to the grade required, and the attention of the student is called to the fact that working for commercially pure xylene is a somewhat difficult matter. This product is a mixture of ortho-, meta-, and para-xylenes, and varies a little in test. A frequent requirement is, boiling-point 136·5° C., 95 per cent. off at 139·5° C., and another, boiling-point 136° C., 90 per cent. off at 139·5° C. and 95 per cent. off at 140·5° C. Yet another, boiling-point 138° C., 95 per cent. at 142° C.

In making these pure products, great care is necessary as regards the speed at which the still is worked. The steam supply must be so regulated that priming does not take place. The water which is passing through the dephlegmator must be kept at a constant temperature. It is necessary that the material should be thoroughly washed with acid, etc., before charging into the still. The best results are obtained if the still is provided with high-pressure closed steam, so as to reduce the employment of open steam to a minimum.

It is important to bear in mind that if a paraffinoid crude benzole is to be passed through the plant for the purpose of working for commercially pure benzene, etc., then great care must be given to the operations of washing, distillation, and dephlegmation. In regard to washing with acid, this must be more drastic than usual, and it will naturally involve a larger loss, chiefly in removing unsaturated paraffinoid bodies. Distillation must be carried on at a very slow rate during the working off of fore-runnings and intermediate fractions (a process known as "sweating off"), and greater attention to dephlegmation is necessary. It will be found that the "change over" points will be less definite, and on this account a larger amount of fore-runnings and intermediates will be obtained than with a crude benzole which is practically free from paraffin bodies. Also it should be noted that the commercially pure distillates will not be paraffin free.

For the guidance of the student the following average figures, showing the cost of labour, chemicals, and steam to produce 1 gallon of rectified material, are given. It must be clearly understood that figures like these will vary in different works according to local conditions, state of the chemical market, etc. To produce 1 gallon of 90's benzole, 0·48d.; 1 gallon of 90 per cent. at 160° solvent naphtha, 0·56d.; and 1 gallon of heavy naphtha, 0·59d. These are pre-war figures, and in order to bring them up to present-day standards the necessary percentages for increased labour charges, etc., must be added.

Some useful information on the temperature of spontaneous ignition of mixtures of benzole and petrol is given by H. Moore in the *Gas Journal.*[1] The following table gives the ignition-points of some of these mixtures :—

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[1] *Gas Jour.*, 1920, 149–245. See also *J.S.C.I.*, 1920, 217A.

Benzole per cent.	Petrol per cent.	Ignition point.
100	0	630° C.
90	10	481° C.
80	20	303° C.
70	30	290° C.
10	90	283° C.
0	100	272° C.

An interesting and useful chapter on " Benzole as a Motor Fuel " will be found in Whitehead's *Benzole,*[1] to which the reader is referred. Additional particulars will be found in a paper by J. C. Mackie.[2]

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[1] Benn Bros., Ltd., 8 Bouverie Street, London, E.C. 4. 12*s*. 6*d*. net.

[2] " Use of Benzole and Benzole Mixtures as Motor Fuel," *Canadian Chem. Jour.*, 1919, 3, 295–297. See also *J.S.C.I.*, November 15th, 1919, 808A.

CHAPTER XV

PLANT FOR THE WORKING UP OF PYRIDINE FROM PYRIDINE ACID

THE plant required for the working up of pyridine acid for pyridine will be dealt with under two heads, viz. : (*a*) That required for the manufacture of crude pyridine, and (*b*) that for the manufacture of rectified pyridine. Dealing with the plant for the manufacture of crude pyridine, there are several methods in vogue. One of these is to manufacture the crude pyridine during the process of making ammonium sulphate. This process requires a plant similar to that used for the manufacture of the latter material, as far as the still, liming apparatus, saturator, or cracker box, etc., is concerned. The cracker box is charged with diluted and clarified pyridine acid of a strength of about 50° Tw. instead of diluted B.O.V. A connection is fitted to the cracker box to conduct away the aqueous pyridine vapours that distil off owing to the heat of chemical reaction between the ammonia and the sulphuric acid, which is in loose combination with the pyridine bases. These vapours are conducted to a suitable condensing coil, and from there to a pyridine water-tank, and the poisonous non-condensable gases are conducted away for treatment by one of the approved methods. The weak pyridine water is allowed to rest, any oil which separates is skimmed off, and the pyridine water is then distilled until about one-third of its volume has been collected. From this point the plant and process resembles that described in this and the following chapter.

For the working up of pyridine acid by a more general process than that just described, the following pieces of apparatus are required : Lead-lined wooden tanks for the dilution of the pyridine acid ; a large egg ; a still constructed of wrought iron or mild steel and provided with suitable fittings ; a condenser coil and tank ; a pyridine water-receiving tank ; a pyridine springing and drying tank ; one or more caustic soda tanks ; a lime mud tank ; and suitable staging, tackle, etc.

The lead-lined tanks, or tanks for dealing with the pyridine acid, may be of any suitable shape, and constructed of wood or mild steel, lined with, say, 5 lb. or 7 lb. chemical lead. If convenience will allow, they should be fairly deep, in order to render easier the skimming off of the resinous matter which comes to the top during the process. They may be erected on the ground level, and provided with a connection near the bottom for running off the clear pyridine acid into the egg.

The egg may be constructed of wrought iron or mild steel, and, if desired, lead-lined. In the author's experience a mild steel egg has proved quite suitable, and very little corrosion seems to take place, provided it is well drained and steamed out after each operation. The size of the egg will vary a little, according to the bulk of material which has to pass through it ; but a good average capacity is 400 gallons. It should be provided with a pressure gauge ; safety-valve ; a 1-inch air inlet ; a 1-inch steam inlet ; a 2-inch outlet-pipe, which dips into a small dish made in the lower part of the egg and almost touches the bottom ; a 2-inch pyridine acid inlet ; and at the bottom on one end a 1-inch drain-pipe and valve.

In order that the diluted pyridine acid may run into the egg by force of gravity, this piece of apparatus should be erected just below ground level. It is advisable to dig a sump deep enough to allow a three-gallon bucket to be placed below the drain-pipe. The hole into which the egg is placed, and also the sump, should be brick-lined, and just sufficient space allowed in order that the sides of the apparatus may be inspected : about 4 inches clearance is sufficient. It is advisable to keep this piece of apparatus just off the bottom, supporting it at intervals on non-absorbent bricks which have been treated with an iron protective compound. It is a good plan to coat the whole of the outside of the egg with a bituminous iron protective paint, to prevent rusting.

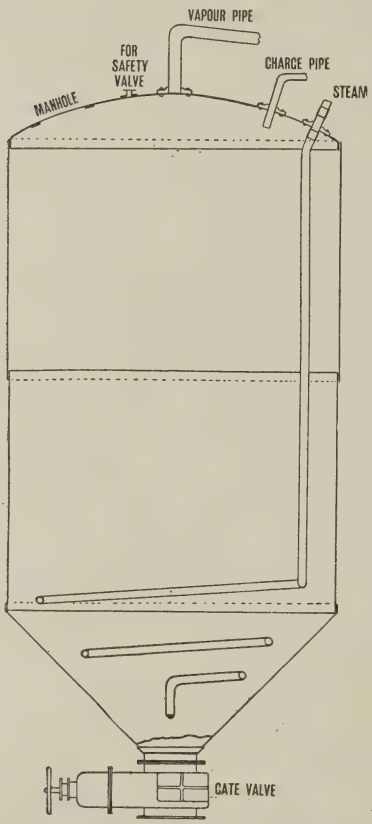


Fig. 106.—Still for the Distillation of Neutralised Pyridine Acid.

For the distillation of dilute and neutralised pyridine acid, a still (Fig. 106) constructed of wrought-iron or mild steel plates, about $\frac{1}{2}$ inch thick, is quite suitable. The bottom of the still may be dished, or, better, of the shape of an inverted cone. At the bottom of the dish or the apex of the cone a 12-inch treacle valve or gate valve is fitted. It will be found that a still with a cone-shaped bottom will discharge the lime mud easier than any other shape. The dome of the still is constructed with a slight rise, and on its centre is fitted a cast-iron swan-neck stool and swan neck. If desired, however, a 3-inch wrought-iron pipe may be used instead of the swan neck and swan-neck stool for the purpose of conducting the vapours to the condensing coil. A manhole 18 inches by 12 inches and a draw-up lid must be arranged for on the dome of the still. The charge-pipe will enter the dome of the still and should project a little on the inside ; close to the point of entry should be fitted a cast-iron gland cock. A steam-pipe also enters the dome and runs almost to the bottom, where it is connected to an open steam coil. This coil will have to be arranged according to the shape of the bottom ; it is advisable to place it as near the bottom as possible, and also, if it can be managed, to arrange for two laps. The diameter of this coil and the steam-pipe supplying it will vary according to the size of the still. As a precaution, a small safety-valve of suitable type may be fitted to the still dome, or to the swan neck. In order to wash away any lime slurry which may lodge on the bottom, particularly near the steam coil, it is as well to provide a 1-inch or $1\frac{1}{2}$-inch water supply, to which may be connected a piece of flexible hose. After the still has been discharged and is cool, water may be played by means of the hose through the manhole, and by this means the still can be washed out thoroughly after each operation.

Connected to the vapour pipe of the still is a condenser coil, composed of a number of laps of wrought-iron pipe, circular in plan. This coil will vary in diameter according to the size of the still to which it is fitted. For instance, a still of a total capacity of about 1,500 gallons would require a condensing coil of 3 inches in diameter and about 150 feet long. The distance between each lap should be not less than 4 inches, in order to allow a free circulation of water, and the distance between the edge of the condenser coil tank and the outside edge of the coil about 6 inches. A cylindrical wrought-iron tank constructed of $\frac{1}{4}$-inch plates is used to contain the coil. This tank is provided at the top with a water outlet and a water supply pipe, which should reach to within about 2 inches of the bottom. The end of the condenser coil may be put either through the bottom or the side of the tank, and is connected up to a delivery direct into the pyridine water receiver. It is as well to place at the bottom of the condenser tank a 1-inch drain tap, in order that the water may be removed if the tank or the coil require repairing.

For the collection of the pyridine water which runs from the condenser coil, a square, cylindrical, or rectangular tank may be used, according to convenience. This tank may be constructed of wrought-iron or mild steel plates, and covered in at the top with a wooden cover, which can be easily removed. It must be provided with a 2-inch run-off tap. In many cases it is convenient to use this receiver for the purpose of separating the pyridine from the water and afterwards drying it. If it is not convenient to do this, then a further tank will be required. This tank will, of course, have to be connected to the receiver and provided with two 2-inch run-off taps, one for the removal of spent soda and the other for dried pyridine, and also an inlet pipe to convey caustic soda to the contents of the tank during the drying operation. It may be constructed of mild steel plates, or of wood, lead-lined.

In the process of drying pyridine, strong caustic soda lye is required, and it is necessary to provide a tank for holding this. A further tank will be required, into which the dilute caustic soda lye may be run after the operation. If solid caustic soda is used to prepare the strong solution, then the strong lye tank must be provided with a grid, the bottom of which must be just covered with water when the tank is, say, three-parts full. This grid is required to support the split drum of solid caustic soda. The process of dissolving will go on mechanically, especially if a small open steam coil is placed in the tank and the water warmed. Some manufacturers prefer to use liquid caustic soda of 90° Tw. If this material be employed, then it is not necessary to place a grid in the strong lye tank, as this quality of soda may be run out of the drums into the tank. In order to transport the strong caustic soda lye into the pyridine drying tank, an egg or blow boiler is required (some prefer to use a pump, but this plan cannot be recommended). If convenient, the weak pyridine acid egg may be employed for this purpose. If this method is not convenient, then a rather smaller egg may be put in.

A tank is required into which the lime slurry from the pyridine still may be run after the completion of an operation. This tank should be placed immediately underneath the still, and constructed of sufficient size to contain with ease the whole of the lime slurry from one operation. As this slurry is generally very wet, and a certain amount of water is dropped on to it during the washing down of the still, it is a good plan to build into the tank a filter bed, similar to that described in the manufacture of caustic soda (Chapter X, page 220). This will materially assist in the separating of the water from the slurry. The slurry is dealt with in a very similar fashion to the lime mud from the causticisers, and should it be necessary, owing to circumstances, to produce a very stiff mud before removing from the works, then a centrifugal machine may be required to deal finally with the material.

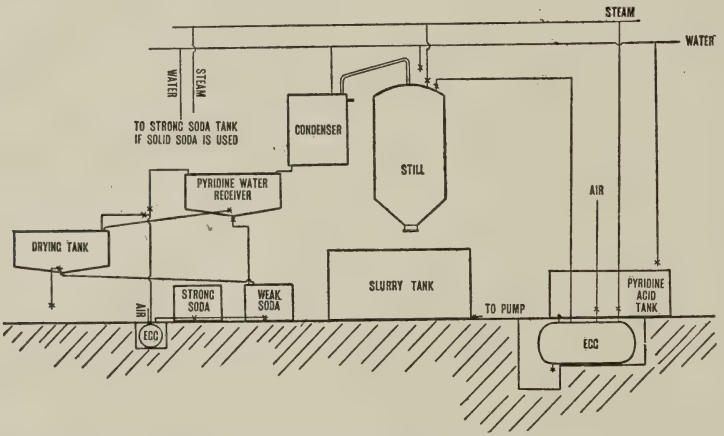


Fig. 107.—Diagrammatic Illustration of One Method of arranging a Recovery Plant for Crude Pyridine.

With reference to the position of the various pieces of plant described, it is necessary that the still be erected of sufficient height to allow the condenser coil and tank, and also the pyridine water and drying tanks and the lime slurry tank, being placed above ground level. The pyridine drying tank should be of such a height from the floor that drums, carboys, or barrels may be filled from it by force of gravity through the run-off tap. The lime slurry tank may be placed on the ground level, or a little above it, according to convenience. The caustic soda tanks should be on the ground level, and the egg, if one is put in for dealing with the caustic soda lye, placed in close proximity to the tanks and just below ground level. Over the caustic soda tanks and the pyridine drying tank a runway is erected, on to which a chain block and pulley is fitted for the purpose of hauling up caustic soda drums, etc. Necessary staging, made of iron, may be erected round the tanks for the convenience of the workmen attending the process. Fig. 107 shows diagrammatically one method of arranging the plant.

For the rectification of crude dried pyridine, the following are the chief pieces of plant required: A wrought-iron or mild steel still with fittings; fractionating tower; condenser coil and condenser tank; receiver or receivers (some prefer working into small drums or carboys), and one or more bottoms tanks.

The still may be constructed of ½-inch plates. The bottom is best built concave and connected to a channel plate in a similar manner to that described under tar stills. A suitable run-off or tail pipe is fitted to the still for the discharge of bottoms. The dome of the still should have a slight rise, and in the centre of it a swan-neck stool and swan neck are fitted. A charge-pipe is connected to the still at the top, and it is also provided with a manhole and draw-up manlid. It is advisable to fit a safety-valve to the still. The still settings, flues, fire-place, etc., are built in a similar fashion to that described under tar stills; but it must be borne in mind that the top of the flue must be just below the level of the liquid left in the still at the finish of the operation, otherwise there is a risk of the still plates getting burnt.

Connected with the swan neck is a small fractionating tower or column. This tower may be cylindrical in shape and built of wrought iron, and inside a series of perforated plates are fitted. The number of these plates need not be large, say, between 10 and 15. One constructed on a similar plan to that shown in Fig. 98 will prove quite suitable. The column is provided at the bottom with a U return pipe, which is led into the still, and at the top with a vapour pipe which is connected to the condenser coil.

With reference to the condenser coil, this is best constructed of lead. It should be properly stayed inside the condenser tank, which is constructed of wrought iron. The usual water supply and outlet arrangements and drain tap are fitted to the tank. The end of the coil is connected to a small observation tank, which may be constructed of wood and lead-lined, and provided with an outlet, which may lead to receivers, or through which the distillate can be run into carboys or drums.

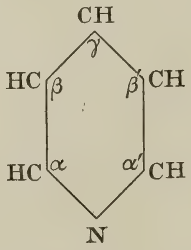
Tanks for the storage of still bottoms may be constructed of wrought-iron or mild steel plates, and built of any suitable shape. They must be covered and provided with a manhole and lid, charge-pipe, discharge-pipe, and air outlet. The latter is necessary to let out the air when running in the bottoms. These tanks may be placed in any suitable position near the still, according to convenience.

CHAPTER XVI

THE RECOVERY AND RECTIFICATION OF PYRIDINE BASES

Pyridine bases as recovered from coal tar consist of a mixture of aromatic bases corresponding to the general formula CnH_2n-_5N, of which the chief are pyridine, picolines, lutidines, and collidines.

Pyridine, C_5H_5N, is a colourless, mobile liquid, possessing a peculiar, unpleasant odour. Its specific gravity at 0° C. is 1·0033, at 15° C. 0·9855, and at 25° C. 0·976. It forms colourless crystals which melt at less than $-100°$ C., and it boils at 116° C. (corr.). In water, alcohol, and ether it is soluble in all proportions, and it turns red litmus blue. Pyridine is represented by the following constitutional formula :—



It is very stable towards oxidising agents such as nitric and chromic acids, even when boiling, and is only with difficulty attacked by the halogens. If heated to 330° C. with a mixture of concentrated nitric and sulphuric acids, β-nitro-pyridine is formed, in the shape of colourless, needle-like crystals possessing a melting-point of 41° C. and boiling at 216° C. Boiling with concentrated sulphuric acid yields a sulpho compound.

Pyridine is a strong tertiary base, and it forms crystalline salts with one equivalent of a mineral acid such as the sulphate $(C_5H_5N)_2$, H_2SO_4, and the hydrochloride, C_5H_5N,HCl. With platinum chloride it forms a double salt, $(C_5H_5N,HCl)_2PtCl_4$, which crystallises in orange-yellow needles, melting at 240° C. and dissolving with ease in water. On prolonged boiling this solution deposits a very sparingly soluble yellow salt of the formula $(C_5H_5N)_2PtCl_4$. Pyridine reacts with methyl iodide, forming pyridine methiodide, C_5H_5N,CH_3I, and, like ammonia, it blackens mercurous chloride. When pyridine is added to a solution of ferric chloride it gives a precipitate of ferric hydrate.

Pyridine, if pure, can be readily sulphonated by heating it with sulphuric acid in the presence of vanadyl sulphate.[1] Pyridine forms a loose combination with phenol, known as pyridine-phenoxide, having the formula C_6H_5OH,C_5H_5N.

According to Mackenzie[2] pyridine forms a definite hydrate with water, which boils at 94·4° C.

Goldschmidt and Constam,[3] on examining a mixture of bases obtained from a coal tar distillate, discovered a molecular compound of pyridine and water having the formula :—

$$C_5H_5N,3H_2O,$$

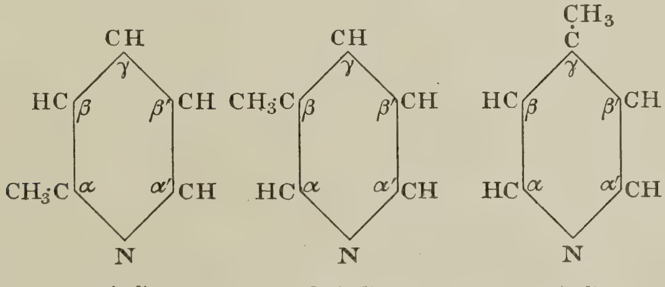
This substance possessed a specific gravity of 1·0219, and a boiling-point of 92° to 93° C.

On a very energetic reduction with hydriodic and at 300° C., pyridine yields normal pentane and ammonia.

Hans Meyer and Alice Hoffmann-Meyer[4] finds that pyridine is decomposed when exposed to a temperature corresponding to bright red heat, yielding mainly 2 : 2′—dipyridyl having a melting-point of 69° C., and also small quantities of 2 : 3′—and 2 : 4′—dipyridyl.

Pyridine in comparatively dilute solutions (1 : 700) has the power of coagulating albumen, and it is stated by some that on this account it possesses strong bactericidal properties. The author disagrees with this on account of a large number of bacteriological experiments which he carried out on disinfectants which contained pyridine bases, giving low results when examined by the Rideal-Walker test.

The three picolines or methyl pyridines, $CH_3{\cdot}C_5H_4N$, possess many properties in common with pyridine. They are represented by the following constitutional formulæ :—



α-picoline. β-picoline. γ-picoline.

The first or α-picoline has a specific gravity of 0·9613 at 0° C. and of 0·9526 at 10° C. It boils at 133·5° C. (corr.), and is oxidised by potassium permanganate to picolinic acid, $C_5H_5N{\cdot}\alpha COOH$. The β-picoline possesses a specific gravity of 0·9762 at 0° C., and it boils at 143·5° C. On oxidation it yields nicotinic acid, $C_5H_5N{\cdot}\beta{\cdot}COOH$. The last of these isomers, γ-picoline, has a specific gravity of 0·9742 at 0° C., it·

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[1] Ger. Pat. 160,104.

[2] *Jour. Ind. Eng. Chem.*, 1909, p. 360.

[3] *Berl. Ber.*, 1883, p. 2976.

[4] *Jour. Pr. Chem.*, 1921, 102, 287–294.

boils at 142·5–144·5° C., and on oxidising is converted into isonicotinic acid, $C_5H_5N{\cdot}\gamma{\cdot}COOH$.

There are six isomeric dimethyl pyridines or lutidines $(CH_3)_2C_5H_3N$, five of which have been discovered in the bases from coal tar. These are : $\alpha\ \alpha'$ lutidine, having a specific gravity of 0·9420 at 0° C., and boiling at 142°–143° C. ; $\alpha\ \gamma$ lutidine, with a specific gravity of 0·9493 at 0° C., and boiling at 156°–157° C. ; $\alpha\ \beta$ lutidine, possessing a boiling-point of 162°–163° C. ; $\alpha\ \beta'$ lutidine ; $\beta\ \gamma$ lutidine, boiling between 163°–164° C.

The isomeric trimethyl pyridines or collidines are represented by the formula $C_5H_2(CH_3)_3N$; and 1 ·3 ·5 collidine possesses a specific gravity of 0·917 at 15° C., and it boils at 172° C. (corr.). The 1 ·3 ·4 isomer boils at 165–168° C. (corr.).

The pyridine acid as it is run off from the bottom of the washing tanks contains, in addition to pyridine bases, oily and resinous substances, and it is necessary to separate these substances before the pyridine can be recovered. This is done by adding clean water, with thorough stirring, and the amount added is, as a rule, about the same bulk as that of the pyridine acid. Some prefer to work to a specific gravity, and if this is done it will vary between 40° and 45° Tw. It should be borne in mind that unless sufficient water is added, some of the oil and resinous matter may be retained in the pyridine acid, and if this does happen the whole batch of crude pyridine will be spoilt. It is far better to slightly over, than under, dilute the pyridine acid. A point worth bearing in mind is that sometimes the first wash water (after the acid washes) from the benzole and naphtha may contain some pyridine bases, and therefore this water may be used with advantage to dilute the pyridine acid.

After the addition of the water, and a thorough stirring, the contents of the tank are allowed to rest for some hours. It is advisable, if it can possibly be managed, to allow the contents of the tank to rest overnight ; the longer the period of rest the more complete the separation of oily and resinous matters. When these substances have completely separated, they are skimmed off the subnatant clarified pyridine acid. Should the mass be heavy and resinous in nature, it is usually burned at the steam boilers. If, however, it is oily and will flow, it may be mixed with creosote oil, or if it appears to be composed to a large extent of unaltered benzene hydrocarbons, then it may be mixed with crude oils. If it is mixed with creosote or crude oils, care must be taken that no acid liquor is removed with it.

It is wise to submit a sample of pyridine acid to a test in the laboratory to see whether it is saturated with pyridine bases. If it is not, it may be used as a first wash on a fresh oil, after it has been diluted a little, and the oily and resinous matter skimmed off. By this means a further quantity of pyridine bases will be taken up, and generally a complete saturation obtained, at the same time very little oily or resinous matter is picked up. Pyridine acid of this nature must, however, be put through the same process of dilution as that already described before working up for the recovery of bases.

A useful point to bear in mind is that the condensed water from a steam distillation of once-distilled light oil contains some pyridine bases. When it is convenient, this water should be used to dilute the pyridine acid. The following details of an actual distillation will illustrate this point :—

Once-distilled light oil charged into the still and submitted to distillation by steam, the volume being 1,200 gallons.

Time.	Rate of distillation.		Pyridine bases in water.
	Water.	Oil.	
Hour.	Gall. per hour.	Gall. per hour.	Per Cent.
1st	1	100	1·3
4th	25	75	1·5
9th	45	50	0·65
12th	55	20	trace

Volume of pyridine bases in the bulked water, 2·73 gallons.

Amount of pyridine bases removed from the oil by water, 0·228 per cent.

The clarified pyridine acid is run from the bottom of the diluting or treatment tank into the acid egg. In the meantime the still is charged with a quantity of quicklime. The quicklime is slaked while in the still, and the mass thoroughly boiled up with open steam, the manlid, of course, being closed prior to the boiling operation. When the lime-milk is thoroughly heated, the pyridine acid in the egg may be blown into the still. The pyridine acid should not, under any circumstances, be introduced into the still first, as owing to its more or less acid nature it is apt to act upon the metal, and also as the reaction with lime commences at once the addition of this material last will make the operation obnoxious and may result in some loss. It will generally be found that the distillation commences almost as soon as the contents of the egg have been discharged into the still, and on this account care must be taken when introducing open steam into the still, otherwise there is a risk of blowing over some of the contents into the coil and receiving tank. The water flow through the condenser tank must be started before charging the pyridine acid on to the lime-milk. Immediately the acid egg is discharged it is advisable to open the drain cock and thoroughly drain, and then cleanse by blowing open steam into the egg for a short time.

The rate of distillation is controlled so that the distillate (which consists for some considerable part of the operation of a solution of pyridine bases in water) flows from the worm end in a stream about the thickness of three fingers placed together. This distillate should leave the condenser coil at the beginning perfectly clear, not cloudy. There are times when a slight cloudiness appears, which clears up in, say, about ten minutes. If, however, the cloudiness persists for any considerable length of time, then it is an indication that an excess of oily matter has got into the still with the pyridine acid. In a case like this, there is nothing to do but finish the distillation and recover the pyridine, as will be described shortly, dissolve it in dilute acid, and allow the oil to separate and then skim off, after which the clarified pyridine acid will have to be submitted to another distillation. Towards the end of the distillation it will be noticed that the distillate leaves the worm end cloudy. This cloudiness is not due to oily material, but to heavy pyridine bases which are not soluble in water. These bases are worth recovering, but are not so valuable as the soluble ones, and the distillation is continued for some little time after the appearance of the cloudiness which indicates their presence. The best method of obtaining the point at which the distillation should be discontinued is to examine by a rough test a sample of the distillate as it leaves the worm end for the percentage of pyridine bases. This test is carried out as follows. Two hundred c.c. of the distillate are run into a separating funnel and "sprung" with about 80 c.c. of 90° Tw. caustic soda. After a short rest the under-lye is removed and a further quantity of 90° Tw. caustic soda (about 50 c.c.) added. The lot is well shaken, allowed to rest, the under-lye removed, and the bases run into a graduated measure.

If it is desired to recover all the heavy bases possible, then the distillation should cease when about $\frac{1}{2}$ per cent. is present in the distillate; otherwise the operation is brought to a close when 1 per cent. of bases are present in the distillate as it runs from the worm end. The length of time which a still may run between 1 and $\frac{1}{2}$ per cent. is sometimes considerable, and it may cost in many cases more for steam, etc., than the heavy bases which are recovered are worth. In addition to this, there is such a large volume of water distilling into the pyridine water tank that a very considerable amount of soda will be required to throw the whole of the pyridine bases up, and this will result in a very weak recovered caustic lye, which may require concentration before it can be used in the works for any other purpose. With further reference to this point, some distillers prefer to collect heavier bases in a separate tank and spring them separately with soda. Throughout the whole operation the distillate should leave the worm end at a temperature below 75° F.

Details of an actual working will, no doubt, be of use to the student.

Charge of diluted and clarified pyridine acid into still, 350 gallons. Distillation commenced at 12 noon. Pyridine bases in distillate estimated with 90° Tw. caustic soda lye.

Time.	Percentage of bases in distillate at worm end.	Average rate of distillation.	Remarks.
12·15	56	110 gal. per hour	Heavy bases appeared at 1.30 p.m. At 3 p.m. 292 gals. of distillate collected. At 4 p.m. 400 gals. collected.
12·30	48		
12·45	43		
1·00	31		
2·00	10		
3·00	4		
3·45	2		
4·00	1·2 =1·03 dried bases		

It is advisable to discharge the contents of the still through the gate valve at the bottom into the tank underneath very shortly after the operation of distillation is finished. If this is not done, there is a tendency for the lime residue (this consists chiefly of a mixture of calcium sulphate and unreacted-upon lime) to settle on to the still bottom and sides into a dense mass which is difficult to remove. As soon as possible after the discharge of the lime mud, the manhole should be opened and the sides and bottom of the still washed down with cold water. The mud, after draining by filtration or any other method found suitable in the works, is either taken to a " tip " or got rid of in any other convenient manner.

With reference to the quantity of lime required for a distillation of clarified pyridine acid, this will vary somewhat according to the amount of sulphates of the bases present. It is as well to submit a small quantity to an examination in the chemical laboratory for the amount of sulphuric acid, and then calculate the quantity of lime required for neutralisation. A slight excess over this quantity is generally added. As a guide 500 gallons of clarified pyridine acid, at a strength of about 40° Tw., will require 1,600 lbs. of Buxton lime. The author, however, strongly advises a laboratory test to be made each time, rather than working by rule of thumb.

The weak pyridine water in the receiver will contain a varying quantity of pyridine bases. Average amounts range between 35 and 40 per cent. This pyridine is recovered in most works by the addition of caustic soda of moderately high specific gravity. Pyridine bases are not soluble to any appreciable extent in solutions of caustic soda above 30° Tw. It is therefore necessary to use a strength of caustic soda sufficiently high to yield an under-lye of a strength not less than 30° Tw. or 1·15 specific gravity at 60° F. A good strength to use for the separation or springing of the pyridine bases from the water is between 45° and 50° Tw. While adding the caustic soda lye the contents of the tank must be thoroughly agitated, and when this operation is finished a period of resting of, say, one or two hours should be allowed. The weak under-lye may then be run off into a storage tank for further use, say, for the recovery of cresylic acid or phenols, or it may be concentrated or reinforced with solid caustic soda to raise its strength. The pyridine which has separated will yet contain water, and it is necessary on this account to " dry " it.

The pyridine bases are considered as sufficiently " dry " when they contain not more than 4 per cent. of water. The drying process may require several treatments with strong caustic soda, but in all cases the last operation should be conducted with a caustic soda lye of a strength of not less than 90° Tw. In the author's opinion caustic soda for use in the drying operations should not be weaker than 60° Tw. for a commencement. It is not possible to give any definite figures in connection with the volume required to " dry " pyridine bases, but these quantities can be found quite easily by carrying out rough laboratory tests on a given quantity of the bases. If 50 c.c. are taken in a 100 c.c. test mixer, and small quantities of caustic soda of the strength it is desired to use are added, shaking after each addition and allowing to settle until a point is reached where a further addition of the caustic lye shows no further shrinkage of the pyridine bases, then from the amount of caustic soda required to reach this point the volume necessary to " dry " the bases contained in the treatment tank can be obtained by a simple calculation.

In a works where the CO_2 process for the recovery of phenols is in use, the pyridine may be conveniently sprung or separated from the water by the use of soda ash (58 per cent. alkali). It must be remembered, however, that the separated pyridine cannot be dried with this material. The under-lye of soda ash solution can be used for reinforcing the spent liquor (impure carbonate of soda solution) obtained from the reaction tower before it is causticised. (See Chapter VIII.)

This under-lye may also be causticised after diluting to a strength of about 23° Tw. and then used in the CO_2 process or else concentrated and used on the pyridine plant. The soda ash should be added in the dry state, and after each addition of, say, a couple of hundred pounds, the tank contents should be very thoroughly agitated. It is necessary to continue this agitation until the whole of the ash has dissolved, after which the contents are allowed to rest to enable the " sprung " pyridine to rise to the surface. The under-lye of soda ash solution is run off and any drainings removed before the addition of caustic soda for the purpose of drying.

With reference to the quantity of soda ash required to " spring " pyridine bases from weak pyridine water, the following figures may serve as a guide. To every 100 gallons of pyridine water, about 170 lbs. of 58 per cent. soda ash is added: The under-lye, after the separation of the pyridine bases, will test about 40° Tw. If soda ash is used for " springing," the drying operation is carried out in the manner already described.

The " springing " and drying operation may be carried out in the receiving tank, but it is advisable, especially in cases in which a large volume of pyridine acid is to be worked up, to carry out this series of operations in another tank. This will relieve the receiver, and a further distilling operation may be carried on within an hour or so of the finish of the previous one.

The " dried " pyridine may be run into a storage tank to await the process of rectification, or if this process is not carried out at the works, then the pyridine is generally filled into barrels, or, better still, into iron drums, ready for despatch. It is necessary, of course, to sell this material on a test, and the method of carrying this out will be found on page 424, Chapter XXII.

In the process of rectifying crude " dried " pyridine, the fractions are run into small receivers or packages, the former method is the best policy, so that each may be tested at the end of the operation, and a suitable mixing made to obtain a rectified pyridine which will answer any test required by the buyer. The two chief types of rectified pyridine are : One which will give not less than 90 per cent. at 140° C. when distilled in a 100 c.c. Wurtz flask, and the other which yields 50 per cent. up to 140, and 90 per cent. up to 160° C. There are other tests which these rectified pyridines are required to answer, and they will be described fully in Chapter XXII.

Having charged the still with a quantity of crude " dried " pyridine, the fire is lighted, and the temperature of the still contents raised fairly rapidly at first, but as soon as the dome begins to get hot the firing is carefully regulated until the distillate appears at the worm end. Priming into the fractionating column must be avoided.

The distillate is now collected until a sample taken from the worm end and tested does not commence to distil until 140° C. is reached. This fraction may be collected in a single receiver and reserved for 90 per cent. at 140° C. pyridine. If this is done it is advisable to test the contents of the receiver frequently for the percentage at 140° C., after a thorough mixing, when the change-over point is near at hand. The distillation is continued from the point just mentioned until a sample collected at the worm end and tested does not yield anything at 160° C. This fraction is known as heavy refined pyridine.

Another plan may be used for collecting the first fraction from the distillation of crude pyridine. It is to run the distillate into 40–50-gallon drums and cut for the first fraction when a sample taken from the drum into which the distillate is "working" and tested yields about 70 per cent. at 140° C. The second fraction is collected between this point and that at which a sample of the distillate when tested yields nothing at 160° C.

After the second fraction has been collected, distillation is discontinued, and the residue run to the bottoms tank, after an interval of an hour or so, in order to allow it to cool down somewhat. The second fraction is refractionated in the same, or a similar still, in order to obtain some more pyridine bases suitable for mixing with the first fraction. It is advisable to split this fraction on redistillation into two portions, cutting the first fraction when a sample from the worm end begins to distil at 140° C. and the second fraction when a sample tested from the worm end yields nothing at 160° C. The residue in the still is run to the bottoms tank. It is a good plan to collect these two fractions in carboys or small drums, as it renders it more convenient when carrying out the mixing process.

With reference to this process it is not easy to describe in detail the method of carrying it out. It requires a few months' experience in order to decide correctly how many gallons of bases giving one test should be added to bases of another test to produce the desired result. It is a good plan to test the contents of the carboys obtained from the refractionation of the second fraction from the first distillation, and also the contents of the drums which contain the first fraction from the first distillation. Having obtained these distillation tests, experience will teach whether the contents of one or more carboys from the redistillation of the second fraction should be mixed with the first fraction, or whether any of the first fraction should be removed before the mixing is carried out. If it is found that the contents of any of the carboys or drums contain oil, or an excess of water, then they should be rejected for reworking. It is often possible to use pyridine bases containing a fair quantity of water, as the greater part of the distillate is generally free from this substance. If a little oil be present it is generally quite safe to employ for mixing, but it must be used with caution. In the finished pyridine, according to most specifications, water should not exceed 7 per cent., and, when tested according to usual specifications, should show no signs of oil. The methods of testing pyridine bases, both crude and rectified, will be described in Chapter XXII.

With reference to the bottoms, these are sometimes refractionated, and may yield 2 per cent. or 3 per cent. below 140° C. This, of course, is useful for mixing purposes. The distillation may now be carried on up to a point where a sample collected from the worm end and tested yields nothing at about 180° C., and this distillate can be sold as heavy bases. Sometimes the bottoms are sold under the same term without redistillation.

With reference to cleaning the still, it is policy to carry out this operation after every second distillation when working "dried," crude pyridine, and after every distillation when working bottoms or heavy bases.

The following details referring to the yield of pyridine bases from once distilled naphtha and once distilled benzole will no doubt be instructive. The figures are average ones only, and it must be remembered that distillates from different tars will give results higher or lower than them.

Once distilled benzole. 1,100 gallons taken.
One wash only.
Pyridine bases recovered :— Per cent.
8·27 gallons 90 per cent. at 140° C. pyridine bases = 0·75
0·63 gallons higher bases = 0·057

Once distilled naphtha. 1,550 gallons taken.

1st wash.
29·7 gallons 90 per cent. at 140° C. pyridine bases.
8·3 ,, higher bases.
2nd wash.
28·3 gallons 90 per cent. at 140° C. pyridine bases.
8·9 ,, higher bases.
3rd wash.
4·2 gallons 90 per cent. at 140° C. pyridine bases.
1·3 ,, higher bases.
Total. Per cent.
62·2 gallons 90 per cent. at 140° C. pyridine bases = 4·01
18·5 ,, higher bases = 1·19

An average amount of crude pyridine obtained per ton of tar distilled is 0·247 gallons.

CHAPTER XVII

PLANT FOR MANUFACTURE OF CRUDE NAPHTHALENE AND ANTHRACENE

Crude naphthalene and anthracene are not prepared in all tar distilleries, and this remark applies especially to the latter product. It is thought advisable, however, to deal with the subject briefly in this and the next chapter. Crude naphthalene is placed on the market chiefly in three qualities, viz.: drained, pressed, and "whizzed"; and the pieces of plant necessary for the production of these qualities are as follows: Salting-out tanks or boilers, recrystallising tanks, hydraulic presses, centrifugal machines, together with the necessary steam piping, bags, staging, etc.

The salting-out tanks or boilers may be of any convenient shape. Usually they are second-hand steam boilers with the tubes drawn and the ends blanked, or else second-hand egg-ended steam boilers. The size of these tanks or boilers varies generally between 4,000 and 10,000 gallons. Each tank should be provided with a 2-inch inlet pipe; one 2-inch outlet pipe with tap placed at the bottom for the purpose of draining, the outlet being closed inside by means of a lead-lined plug with a long handle, to prevent it getting salted up (this pipe may be connected to a pump if desired, or else arranged to lead the liquid oil into storage tanks by force of gravity); a suitable closed steam coil, built up of 1½-inch steam-pipe; a manhole of the usual size and provided with a loose cover; and also a 2-inch outlet pipe and tap, which may be placed at the bottom of the tank for the removal of the melted salts. Some prefer to put in a by-pass on the draining pipe, and use this for the removal of the melted salts. Others prefer to insert through the top of the boiler a suction pipe reaching to the bottom for the same purpose. Neither of these plans is good. The outlet pipe for the melted salts is connected up to a steam pump, and a pipe line is arranged from the delivery side of the pump, so that the liquid may be delivered into the recrystallising tanks. Reducing T's should be placed on the suction and delivery mains, and connected up to a 1-inch steam pipe, so that steam may be blown through the pipes after the pumping operation, in order to thoroughly clean them and prevent them becoming salted up or choked. The number of salting-out tanks or boilers required will vary, of course, according to the quantity of salty oil it is desired to deal with per day.

Tanks for recrystallising the melted salts should be shallow. A general size is 8 feet wide, 14 feet long, and 2 feet deep. The tanks may be placed on the ground level, or, better, a foot or two above the same, as this will allow air to circulate round them. They are provided with one or more 2-inch outlet pipes and taps, by which to drain away the mother liquor or oil which separates into underground tanks or boilers. The outlet holes should be closed by means of lead-lined plugs, with a handle to facilitate their removal. These tanks must, of course, be under cover, and it is an advantage to arrange that the room in which they are placed can be suitably cooled, or else the tanks themselves may be artificially chilled during hot weather. It may be added that many works do not trouble about chilling at all, but recover just so much salts as will crystallise out at the temperature existing during the time of working.

The salts from the recrystallising tank are removed by manual labour, and either centrifugalled and then pressed in hydraulic presses or dealt with direct for cold pressing in a centrifugal machine. Types of hydraulic press are shown in Figs. 108 and 109. The head, bottom, and table of these presses are of the best cast iron, machined where necessary. Close-grained cast iron is used for the ram, and it is polished the full length to fit the cylinder, which is constructed of best cast steel and supplied with a steel gland. The columns are made of mild steel and fitted with steel nuts. Division plates of mild steel are supplied loose or as part of the press, as shown in Fig. 109.

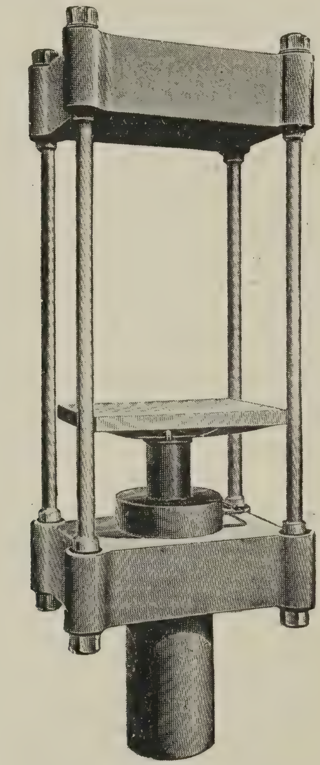
Fig. 108.—Hydraulic Press.

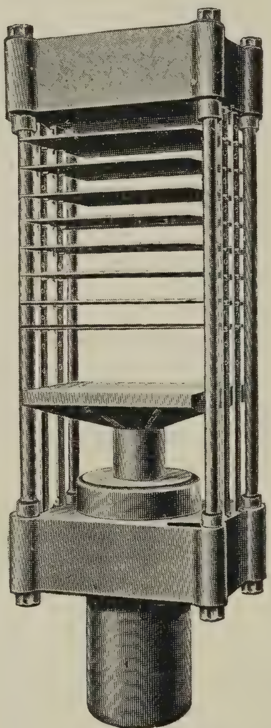
Fig. 109.—Hydraulic Press.

In one type of steam-heated hydraulic press it is so arranged that the plates are built in two portions, one of which is a perforated tray and the other an outer ring which can be supplied with steam. To each outer ring is connected a flexible steam inlet and outlet pipe in order to allow for the upward and downward movements of the plates. There is another type of steam-heated press in which the plates are very similar to those of an ordinary hydraulic press, but on two sides of the press, from the top to a depth equivalent to the space taken by the plates and the charge when the press is run up, are fitted steel boxes or jackets into which steam is led during the pressing operation.

Another type of hot press is cylindrical in shape and consists of the usual press head, press table, ram and columns with round press plates which run in a cylindrical strainer. Enclosing the strainer is a cylindrical steam jacket fitted with the usual steam inlet and outlet pipes.

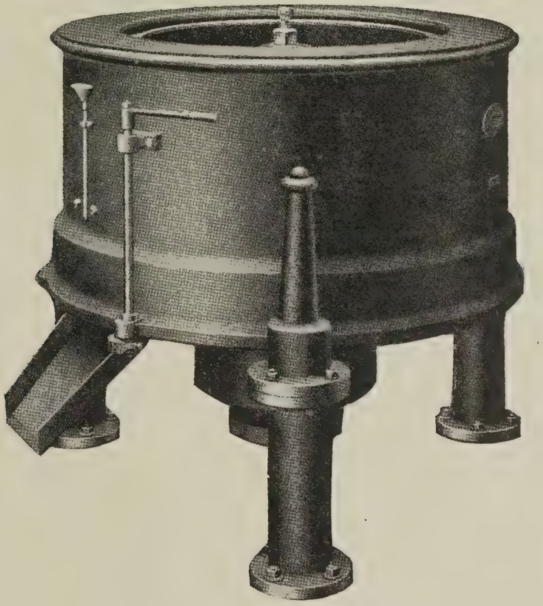

Fig. 110.—Centrifugal Machine.

Centrifugal machines are specially made for this purpose by several firms, and an excellent type, by Thos. Broadbent and Sons, Ltd., is illustrated in Fig. 110. This machine is electrically driven and suspended on three pillars, so arranged that the vibration is absorbed and the necessity for a massive foundation done away with. It is self-contained, the electric motor being built on to the centre spindle. The electric motor is fitted with an automatic starting-gear, which makes the machine foolproof, and the starting up quite automatic. An outlet is provided in the revolving basket through which the " whizzed " material can be discharged down the discharge shoot and on to a small truck or barrow, or into a sack placed underneath. Steam-driven machines are sometimes employed instead of electrically driven ones. It is, of course, necessary to provide an underground tank into which the oil pressed out during the application of hydraulic pressure, or separated by centrifugal force in the "whizzing" operation, can be run.

Further illustrations of centrifugal machines suitable for dealing with naphthalene and anthracene are given in Figs. 111, 112, 113, 114. These machines are manufactured by Pott, Cassels and Williamson. In Fig. 111 is shown a centrifugal and mixer-heater combination. The centrifugal, it will be noted, is driven by a steam engine, the stirring arrangement of the mixer-heater being driven by a belt from a pulley on the engine crankshaft. A steaming apparatus is fixed on the outer collecting case of the centrifugal, and this is used for steaming the inside and outside of the basket, thus keeping its perforations and also the linings clear of any accumulation of paste which may find lodgment there. The mixer-heater is steam jacketed, and the anthracene or naphthalene paste is charged into the mixer, kept stirred, and maintained at a suitable consistence and temperature for being dealt with in the centrifugal drier, by means of the steam jacket and stirrer. If desired two mixers can be provided, so that while one charge is being worked up another can be got ready, thus practically doubling the output of the centrifugal. For instance, a centrifugal with a 42-inch diameter basket, attached to one mixer-heater, will produce 200 lbs. per hour of "dry" anthracene in the form of a fine powder, whilst if a second mixer is provided, so as to have another charge of paste ready for centrifugalising, then nearly 400 lbs. per hour will be "dried."

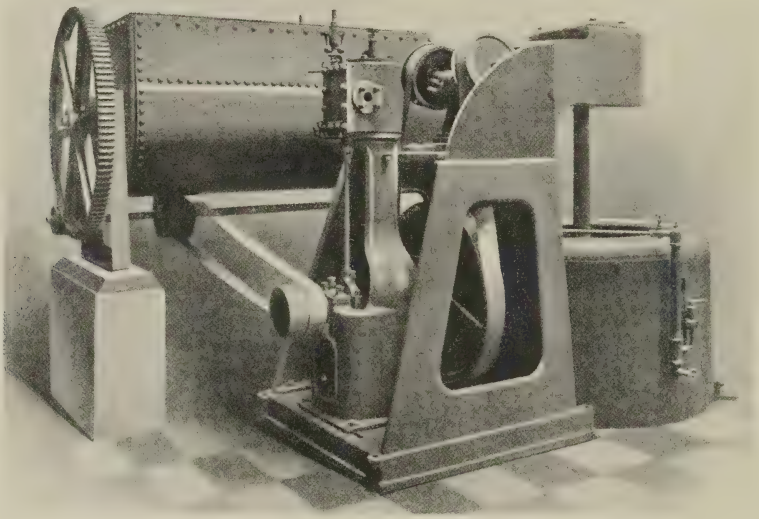

FIG. 111.—CENTRIFUGAL PLANT FOR TREATMENT OF ANTHRACENE AND NAPHTHALENE.
(*Courtesy of Pott, Cassels and Williamson.*)

A centrifugal machine fitted with a basket 36 inches in diameter and attached to one mixer-heater will produce approximately 160 lbs. of "dry" anthracene per hour. It is possible to deal with the anthracene produced from 20,000 tons of tar per annum with a 42-inch centrifugal machine attached to two mixer-heaters.

The output of dry naphthalene by these machines varies a good deal according to the quality of the paste, but the following particulars of the out-turn of three sizes of machine will, no doubt, be useful :—

30-inch machine . . .	112 lbs. to 224 lbs. per hour.
36-inch machine . . .	140 lbs. to 280 lbs. per hour.
42-inch machine . . .	168 lbs. to 336 lbs. per hour.

A sectional view of a centrifugal machine is shown in Fig. 112. When the machine is running the material under treatment assumes the position approximating to the shaded portions in the figure, that is, a vertical wall against the centrifugal basket shell, the liquid substances being expelled through the linings and perforations of the basket against the outer collecting case. From this case the liquid is led by a gutter or pipe to a suitable receiving tank. When the material is sufficiently " dry " the machine is stopped, the discharge valve raised, and the dried powder or crystals, as the case may be, discharged through the bottom of the basket on to a conveyor or barrow placed below.

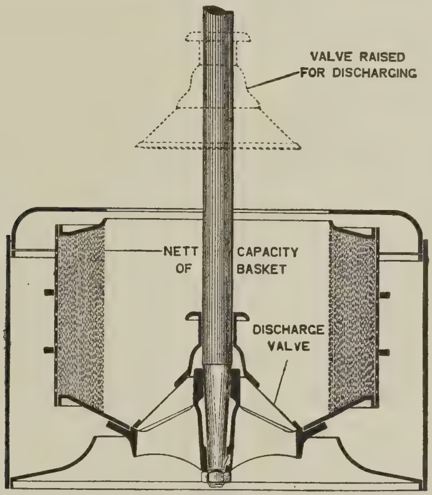

Fig. 112.—Section of Centrifugal Machine (Diagrammatic).
(*Courtesy of Pott, Cassels and Williamson.*)

Fig. 113 illustrates a " Weston " suspended, self-balancing centrifugal which is steam driven. Owing to the fact that this extractor is self-balancing and has no rigid journals, no vibration is communicated to the floor and therefore a special foundation is not required.

A special type of centrifugal machine fitted with a feed hopper, screw conveyor, to remove the centrifugalised material, driving motor, and gear is illustrated in Fig. 114.

A still for use in the process of purification of naphthalene is similar in construction to that of a tar still. An efficient safety-valve must be fitted to the still; one similar to that illustrated in Fig. 27, page 130, will prove suitable, or better, one which can be heated by steam. The condenser coil is best of the spiral form, quite free from elbows, and at the top and in proximity to the bottom a ½-inch steam pipe is inserted by means of a reducing T-piece. This arrangement will enable the stillman to blow steam through the coil, after working, to clean it out thoroughly, and is very useful in case a stoppage should occur. An open steam coil *must* be placed in the condenser tank, as it is necessary to keep the condensing water at a temperature of 85°–90° C. to prevent solidification of the naphthalene. Fuller particulars of still construction will be found in Chapter VI.

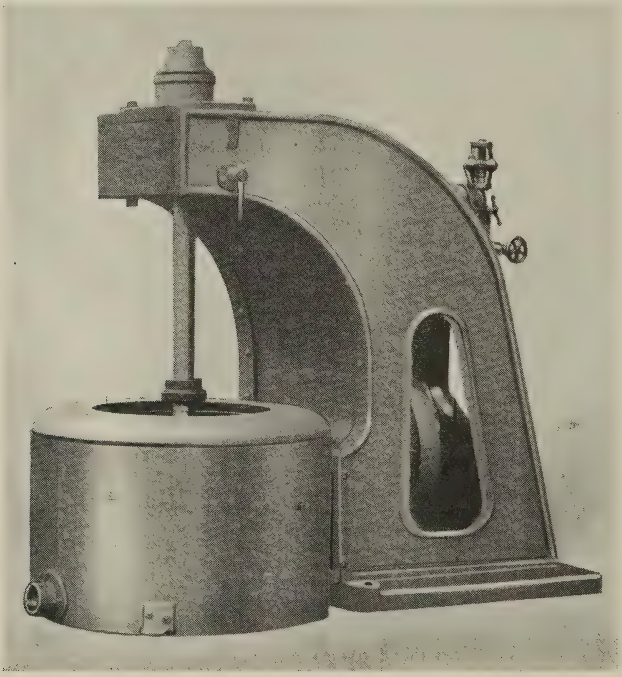

Fig. 113.—" Weston " Centrifugal Machine.
(*Courtesy of Pott, Cassels and Williamson.*)

The methods of working up crude anthracene vary: some prefer to redistil the green oil, others simply to allow it to cool and separate out the crude anthracene. If it is desired to distil the oil before treatment, then it is necessary to put in a still of wrought iron or mild steel, somewhat similar to a tar still in shape, and provided with similar fittings, such as charge pipe, outlet pipe, swan neck and stool, safety-valve, manhole and lid, etc. The rise of the still bottom should not be very great, the crown plate having one of between 12 inches and 18 inches. The concave portion of the bottom is connected to channel plates, as already described under tar stills, and the dome of the still should have a rise of between 12 inches and 14 inches, according to the size of the still. It is, of course, necessary to connect the still to a condenser coil, which latter piece of apparatus will require the usual condenser tank, fitted in all respects as described under tar or light oil stills. The number of receivers will vary according to the desire to separate the distillate into one, two, or three fractions.

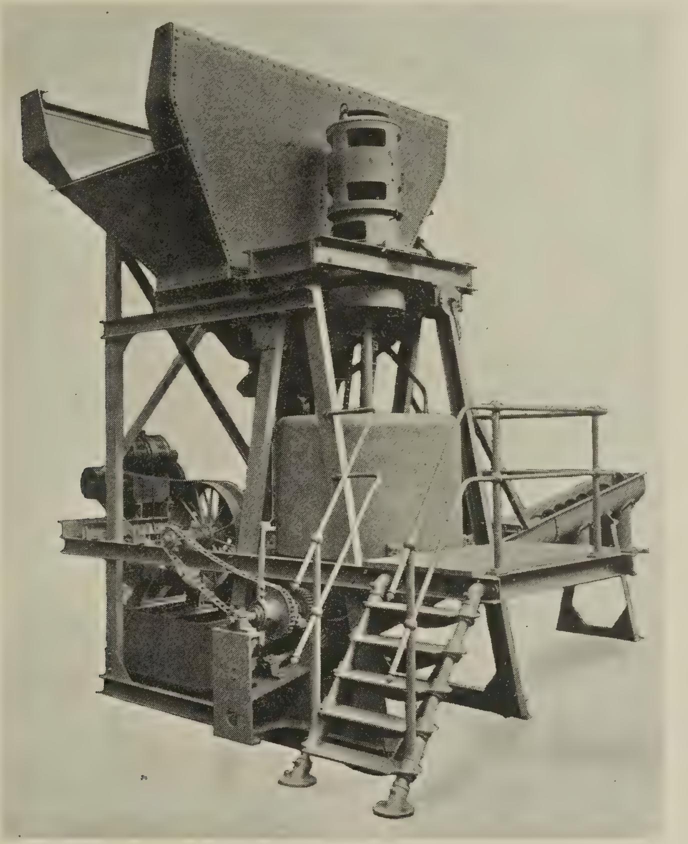

Fig. 114.—Centrifugal Machine.
Showing feed hopper, screw conveyor to remove the treated material, driving motor and gear.
(*Courtesy of Pott, Cassels and Williamson.*)

Whether the green oil or anthracene oil is distilled or not, the remainder of the plant is practically the same. It consists chiefly of shallow, crystallising tanks, about the same size as those used for the recrystallisation of the naphthalene, a filter press or presses, washing tanks, centrifugal machine, one or more hydraulic presses, and a suitable disintegrating machine for reducing to powder the washed and repressed anthracene. The crystallising tanks are fitted with 2-inch pipes and taps at the bottom for the purpose of draining. They should be under cover, and sometimes the chamber in which they are erected is artificially cooled during the summer months. As a matter of fact, the arrangement of these tanks and their fittings is very similar to that already described under naphthalene recrystallising tanks.

If it is desired to press the crude anthracene or crude naphthalene at an elevated temperature, then a horizontal or vertical hydraulic hot press must be installed.

Illustrations of two types of filter presses are given in Figs. 115, 116, and 117 respectively. Fig. 115 is of the flush plate and distance frame type which gives deep chambers. As will be seen from an inspection of the illustration, the plates are square in shape and are fitted with plain bib outlets for the escape of the filtrate.

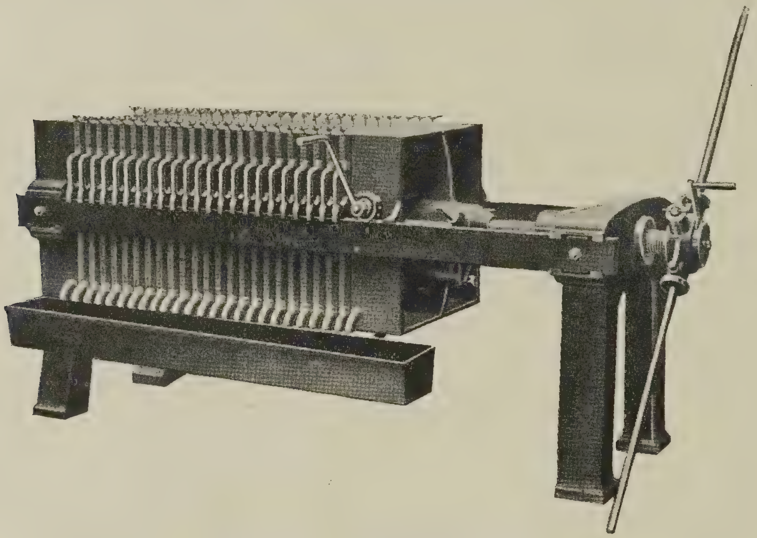

Fig. 115.—Johnson Filter Press.

With reference to the feed inlet, this can be arranged (*a*) through a passage in one corner of each plate having a port to each distance frame, and (*b*) by a central hole through the plates. In order to secure the maximum amount of area of cloth available for effective filtration, careful attention must be given to the filter surface of the plates. Those of the press illustrated have their surfaces studded with small, truncated, square pyramids ; this method, in the author's opinion, forms the most efficient support for the filter cloths.

Fig. 116 illustrates another make of plate and frame press. The plates and frames of this press are provided with a top feed, and to the filtrate outlet of each plate is fitted a cock of cast iron, the plug of which is manipulated by a tommy bar. The filter surface of the plates is formed of rows of small lozenges, the grooves or channels between them being deep, and narrow enough to prevent them being closed by the sag of the filter cloths. In service a press of this type 25½ inches square and making twenty-five cakes each $1\frac{1}{8}$ inch thick handled a batch of 840 gallons of unstrained anthracene oil in two operations, the amount of cake obtained from each operation being 504 lbs. or a total of 1,008 lbs. Experiments showed that the amount of oil in the press cake varied according to the temperature at which the unstrained oil was filtered ; for instance, at 7° C. the press cake contained 49 per cent. of oil, at 15° C. 46 per cent., and at 25° C. 44 per cent. A very good, clear oil was obtained at 7° C., while at 25° C. the filtered oil contained a comparatively large percentage of anthracene salts. The best all-round temperature to work at appeared to be 15° C. The time to fill the press varied from 20 minutes at the medium temperature (15° C.) to 40 minutes at the highest temperature.

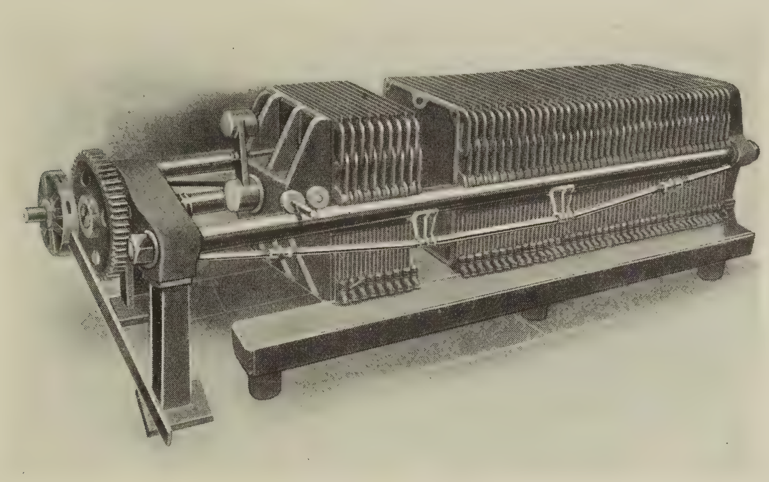

Fig. 116.—Manlove, Alliott Filter Press ; "Plate and Frame" Type.

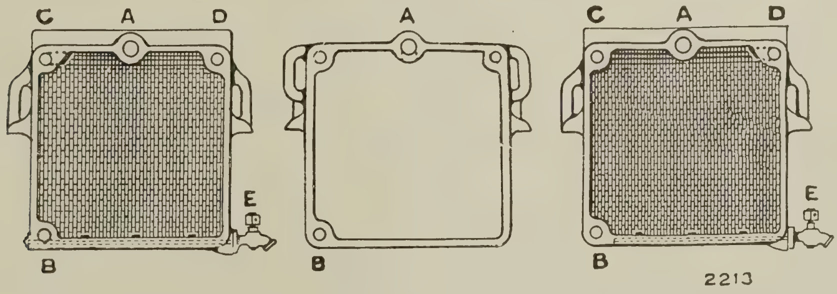

Fig. 117.—Plates and Frame of Manlove, Alliott "Plate and Frame" Type Filter Press.

A, Feed inlet. B, Washing inlet liquid. C, Air outlet. D, Washing liquid outlet. E, Outlet for filtrate.

Fig. 117 illustrates the design of the plates and frames used in the press just described. The wash ports are useful if it is desired to give the anthracene cake a thorough blowing of air in order to displace as much of the remaining oil as possible.[1] To reduce the cakes of hydraulically pressed anthracene to a state suitable for washing, disintegrating machines are the most suitable pieces of apparatus. Among the best types are "Carrs," "Carters," and the "Perplex." Edge runners are recommended by some, but they are slow, and unless the rolls are supported out of contact with the pan are apt to crush much of the anthracene into small masses of thin, hard cakes.

Vessels for washing anthracene are constructed of mild steel and provided with archimedean screw, or one of the various types of paddle agitators. In order to heat the charge they may be fitted with a closed steam coil or a jacket; in the author's opinion the latter is the better method. From the point of view of economising floor space anthracene washers should be of the vertical type. The top of an anthracene washer is best covered in, and a manhole about 24 inches by 12 inches provided, through which the pressed and ground anthracene may be dropped, and by which workmen can enter and leave the apparatus during repairs. A 2-inch inlet is made on the top cover to which a 2-inch charge pipe, for introducing the washing material, is fitted, and at the bottom of the washer a 2-inch outlet is provided, and this is connected to a cock, followed by a wrought-iron main which conducts the contents, after washing and cooling, to a filter press. It may be necessary in some cases to erect a cooling tank in which to allow the material from the washers to cool before filter pressing. Washers of the vortex or Typhoon type are very suitable for dealing with anthracene. Figs. 73, 76, will give a general idea of these.

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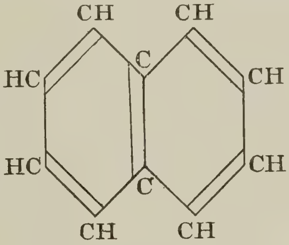
[1] Much interesting and useful matter will be found in Eustace A. Alliott's paper, "Recessed Plate and Plate and Frame Filter Presses," *Proc. Chem. Eng. Group, S.C.I.*, Vol. 11, 1920, pp. 63–88.

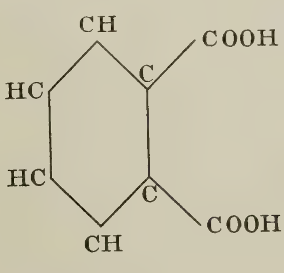
CHAPTER XVIII

MANUFACTURE OF CRUDE NAPHTHALENE AND ANTHRACENE

Naphthalene, $C_{10}H_8$, occurs in the form of white monoclinic crystals possessing a a peculiar tar-like odour. Its specific gravity at 15° C. is 1·1517 and at 100° C. 0·9628. Naphthalene melts at 80° C. (corr.) and boils at 218·21° C. (corr.). In cold water it is quite insoluble, but it is very slightly soluble in hot water. It is dissolved by ether, alcohol, chloroform, carbon disulphide, acetic acid and the essential oils. Toluene and benzene also dissolve naphthalene. At 15° C. 100 c.c. of alcohol dissolve 5·29 parts of naphthalene and at 16·5° C. 31·94 parts are dissolved by 100 parts of toluene. It is represented by the following constitutional formula :—



Naphthalene is a very stable substance and is converted into simpler substances with great difficulty. If it is boiled with dilute chromic or nitric acid it is slowly oxidised into orth-ophthalic acid :—



It is readily acted upon by concentrated nitric acid, forming nitro derivatives, the reaction being facilitated by the presence of concentrated sulphuric acid. If it is heated with concentrated sulphuric acid naphthalene is readily sulphonated, forming naphthalene sulphonic acids. The temperature of the reaction mixture and the strength of the sulphuric acid used determines the number and position of the sulphuric groups.

On adding a cold alcoholic solution of picric acid to a cold alcholic solution of naphthalene a yellow crystalline precipitate of naphthalene picrate, $C_{10}H_8 \cdot C_6H_2(NO_2)_3 \cdot OH$ is formed which melts at 149° C.

The molecular refractivity of naphthalene is (Ma) 43·93. Technically pure naphthalene melts at approximately 79·7° C. Naphthalene exhibits the phenomenon of double refractivity to a marked degree, the resolving power being rather more than 30 per cent. greater than that of Iceland spar.[1]

The following interesting figures showing the solubility of naphthalene in various solvents at 15·5° C., are due to J. F. Smith :—[2]

	Dissolved by 100 parts of solvent.
Benzene (pure)	45·80 parts.
Toluene	32·00 ,,
Xylene	31·50 ,,
Cumene	30·10 ,,
Commercial 90 per cent. benzole	43·20 ,,
Solvent naphtha	31·72 ,,
50 benzene+50 toluene	39·80 ,,
30 ,, +70 ,,	37·20 ,,
50 per cent. commercial benzole	31·80 ,,
Carburine, sp. gr. 0·672	16·90 ,,
Creosote oil, sp. gr. 1·03 (containing 8 per cent. phenols)	9·65 ,,
Scotch blast-furnace oil sp. gr. 0·985 (containing 31 per cent. phenols)	17·64 ,,
Heavy tar oil	8·90 ,,

A few figures determined by the author will be useful for comparison.

	Dissolved by 100 parts of solvent.
Solvent naphtha, sp. gr. 0·872	32·50 parts.
Heavy naphtha, sp. gr. 0·909	25·00 ,,
Petroleum oil, sp. gr. 0·885	11·20 ,,
Scotch blast-furnace oil, sp. gr. 0·956 (containing 3 per cent. tar acids)	17·00 ,,
Cresylic acid, sp. gr. 1·039	15·20 ,,
Heavy tar oil, sp. gr. 1·100	9·20 ,,

Anthracene, $C_6H_4 : (CH)_2 : C_6H_4$, in the pure state occurs in the form of small white glistening plates with a violet fluorescence, which is, however, completely masked by small quantities of impurities. It has a specific gravity of 1·147, melts at 216·5° C. (corr.), and boils at 351° C. (corr.). According to W. Kirby[1] anthracene melts at 218° C. and boils at 340° C. In water it is insoluble, but is dissolved by alcohol, ether, benzene, carbon disulphide, and many other organic solvents. At 15° C. 100 parts of alcohol dissolve 0·59 part of anthracene. In ether it is rather more soluble, 100 parts dissolving 1·17 parts at 15° C.

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[1] W. Kirby, *J.S.C.I.*, February 16th, 1923, 58T.

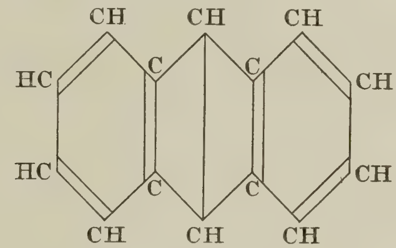
[2] *J.S.C.I.*, 1902, p. 1225.

Anthracene possesses a molecular refractivity of (Ma) 61·15.

The following solubility figures are due to J. H. Hilderbrand, E. T. Ellefson and C. W. Beebe :—[2]

		grams of anthracene dissolved per 100 grams of solvent.			
Alcohol.	Benzene.	Carbon disulphide.	Carbon tetrachloride.	Ethyl ether.	Hexane.
0·328	1·86	2·58	0·732	1·42	0·37

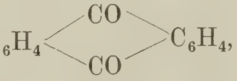
The constitutional formula of anthracene is written thus :—



If anthracene, in xylene solution, is exposed to light it is transformed into dianthracene, which in the dark becomes depolymerised to anthracene. This is one of the rare instances of a reversible photochemical reaction.

$$2C_{14}H_{10} \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} C_{28}H_{20}.$$

It is not possible to nitrate anthracene, and when it is acted upon by nitric acid (and also chromic acid) it is oxidised to anthraquinone $C_6H_4 \langle {}^{CO}_{CO} \rangle C_6H_4$, which melts at 277° C.



When saturated alcoholic solutions of anthracene and picric acid are mixed, ruby-red needles of anthracene picrate, $C_{14}H_{10},C_6H_2(NO_2)_3{\cdot}OH$, are precipitated. These crystals melt at 138° C.

J. E. Zanetti and M. Kandell[3] studied the formation of anthracene from benzene and ethylene by passing the vapours of these substances through a quartz tube, heated to temperatures varying between 800° and 1,000° C. They found the optimum temperature to be 925° C., and at this temperature the yield of anthracene was 0·675 per cent. of the weight of benzene decomposed. Above 925° C. the formation of carbon increased rapidly, while that of anthracene decreased, and at 1,000° C. it ceased altogether.

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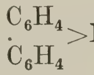
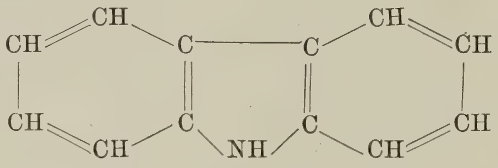
[1] *J.S.C.I.*, 1921, 274T.

[2] *Jour. Amer. Chem. Soc.*, 1917, 39, 2301–2302.

[3] *Jour. Ind. Eng. Chem.*, 1921, 13, 208–211.

Carbazole,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!\!>NH$, when pure, occurs in the form of colourless crystalline plates, which melt, with sublimination, at 238° C. and boil between 354° and 355° C. It is very sparingly soluble in alcohol, ether, chloroform, benzene, and toluene, but much more so in these substances when hot; it also dissolves in cold, concentrated sulphuric acid. Hot, concentrated sulphuric acid converts it into a carbazole disulphonic acid. *In pyridine it is very soluble.* According to Bechi, 100 parts of toluene at 16·5° C. dissolve 0·55 parts of carbazole, whilst at 100° C. 5·46 parts go into solution. Carbazole is a *very* feeble base. With picric acid it forms a stable salt, melting at 182° C., and on heating with caustic potash carbazole-potassium $(C_6H_4)_2NK$, is obtained, which is decomposed by water. It is converted by nitrous acid into nitrosocarbazole $(C_6H_4)_2N{\cdot}NO$, which melts at 84° C. On treatment with sulphuric acid and isatin a blue colouration is produced, and an alcoholic solution of it imparts a fiery-red colour to a pine shaving moistened with hydrochloric acid. The constitutional formula of carbazole is :—



Carbazole occurs in crude anthracene in amounts up to about 20 per cent.

According to W. Kirby's determinations,[1] carbazole melts at 247° C., and boils at 351·5° C.

If to a hot solution of carbazole in pure acetone finely divided potassium permanganate is added, oxidation takes place, and from the reaction mixture two well-defined crystalline compounds and an amorphous substance are obtained. The crystalline compounds appear to be isomeric dicarbazyls, $C_{24}H_{16}N_2$, melting at 220°–221° C., and 265° C. respectively, and the amorphous substance, which is the main product of the oxidation, undoubtedly possesses a high molecular weight. Its constitution has not yet been determined. Neither of the dicarbazyls forms a picrate, and in this respect they differ from carbazole and its homologues.[2]

Phenanthrene, $C_{14}H_{10}$, is an isomer of anthracene, and in the pure state it occurs as colourless scales, exhibiting a pale blue fluorescence. It does not sublime quite so readily as anthracene, melts at 100° C. with some sublimation, and boils at 340° C.

W. Kirby[3] gives the melting-point of phenanthrene as 101° C. and the boiling-point as 332° C. Its specific gravity at 100° C. is 1·063. According to Bechi its solubilities in alcohol and toluene are as follows :—

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[1] *J.S.C.I.*, 1921, 274T.

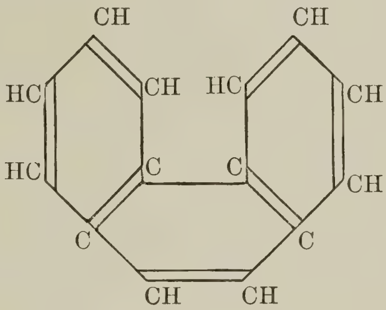
[2] W. H. Perkin, jun., and S. H. Tucker, *Jour. Chem. Soc.*, 1921, 119, 216–225T.

[3] *J.S.C.I.*, 1921, 274T.

100 parts of absolute alcohol at 16° C. dissolve 2·62 parts of phenanthrene.
100 ,, ,, ,, 78° C. ,, 10·08 ,, ,,
100 ,, toluene at ,, 16·5° C. ,, 32·02 ,, ,,
100 ,, ,, ,, 100° C. dissolve phenanthrene in all proportions.

It is insoluble in water, soluble in ether, and also in benzene and carbon disulphide. If picric acid in solution is added to an alcoholic solution of phenanthrene, reddish yellow needles of phenanthrene picrate separate, which melt at 144° C. Treated with concentrated nitric acid it yields nitro compounds, and on heating at 100° C. with concentrated sulphuric acid, *α*-phenanthrenesulphonic acid is formed, whilst if the temperature is raised to between 180° and 190° *β*-phenanthrenesulphonic acid results.

Its constitutional formula is :—



It occurs in crude anthracene in amounts exceeding 40 per cent.

In the manufacture of crude naphthalene, washed light creosote, and also the bottoms from the benzole, naphtha and light oil stills are employed. It is necessary to see that the distillates, such as light creosote, are quite free from tarry matter if they are intended for this purpose. These oils are pumped into the crystallising boilers and allowed to remain for several days in order to crystallise out the naphthalene or "salts."

The contents of these boilers are allowed to rest for a period of time, varying according to the season of the year ; a good average is three to five days. In some works artificial chilling is resorted to, during the summer time or throughout the year, thus reducing considerably the time just mentioned.

When the "salting-out" is completed, the oil which has separated is drained away through the drain-pipes into storage tanks. This oil is tested for its specific gravity, and if found to be low is mixed with liquid heavier creosotes, or strained anthracene oil, and placed upon the market as liquid creosote. The crude naphthalene remaining in the boilers is melted up by the aid of closed steam, and when the whole of it is in the liquid state, and at a temperature well above the crystallising point, it is pumped from the boilers into the recrystallising tanks. Immediately the pumping operation is finished, steam should be blown through the suction and delivery mains, in order to clear them of any liquid salts which may remain and which will, if not removed, solidify in the pipes and cause no end of trouble.

The liquid crude naphthalene in the recrystallising tanks is allowed to cool down and recrystallise out from the oil which has been carried over from the " salting-out " boilers. After a period, varying from two to four days, the drain taps are opened to allow any oil which has separated to run off. This oil is removed to storage boilers or tanks, and allowed to rest for several days, after which it is mixed with other liquid creosote oils and disposed of as liquid creosote. It may be added that any " salts " which is deposited in these boilers is melted up from time to time and pumped into the recrystallising tanks. After the crude naphthalene has thoroughly drained it may be placed into barrels or other suitable packages and disposed of as drained naphthalene.

If, however, it is desired to prepare from the drained naphthalene a quality known as " whizzed " naphthalene, it is removed from the recrystallising tanks and charged into centrifugal machines. Care must be taken to level the " salts " in the cage of the machine, otherwise there is a great risk of wobbling, which may lead to an accident when the machine is set in motion. The cage must not be overcharged, not must it be started up too suddenly. With a good centrifugal it is possible to " whiz " four to six charges per hour, the size of the charge, of course, varying according to the dimensions of the centrifugal. Should the centrifugal be self-discharging, then the " whizzed " crude naphthalene may be released from the bottom into a special receiving pan, or direct into sacks. The oil as it flows from the machine is conducted into the liquid creosote storage tanks or boilers. Centrifugalled naphthalene will contain about 2 to 4 per cent. of expressible oil.

Pressed naphthalene is prepared by taking the recrystallised crude crystals from the recrystallising tanks, " whizzing " them and then placing them into press bags and submitting them to hydraulic pressure. The press bags are made of various materials, sometimes even ordinary sacking being used. The size of a bag when filled will vary according to the dimensions of the press, but an average may be taken as 9 inches wide, 18 inches long, and 3 inches thick. Care must be taken to keep the thickness of the filled bags as even as possible, otherwise there is a risk of rupturing the press table during the process of pressing. When charging, the press table is run down to the floor of the press. It is then covered with bags, arranged so that there is a space of about 2 inches between each. When the table is full, a wrought-iron plate about ¼ inch thick is placed upon the top of them, and this is covered with bags in a similar manner to the table. This operation is carried out until the press is charged. It is important that care be taken to arrange the plates and the bags on them so that they just cover one another, and do not project on any side. Any unevenness vertically will produce what is known as " shunting," *i.e.* the middle will bulge out on one side or the other. This will not only produce some half-pressed material, but there is a very great risk of the press table fracturing. In some types of hydraulic press the plates are suspended from the press-head by steel links, and when the press is run down this results in the plates being of sufficient distance apart to charge with filled bags. If a press of this kind is used, it is necessary to place the bags on each plate so that they cover those on the plate immediately underneath.

When the operation of charging is completed, hydraulic pressure is applied, and the press gently run up. The pressure is then slowly increased until it indicates between 1½ to 2 tons to the square inch. After an interval of about one hour, the hydraulic pressure is released and the press discharged. On opening the bags and removing the pressed cakes, should any wet edges be noticed, these are cut off and repressed with another batch. The cakes of pressed naphthalene are now charged into a disintegrating machine, and when thoroughly broken up placed into packages for dispatch.

A far better quality of pressed crude naphthalene is obtained by using a steam-heated hydraulic press and carrying out the process known as "hot pressing." A naphthalene which has been properly hot pressed will give very little trouble in the refining process and will yield an excellent finished product. It is very necessary to pay attention to the regulation of the temperature employed for pressing. Within limits the higher this temperature the better the result, as more foreign matter is removed, but it must not be forgotten that the presence of oil in the unpressed naphthalene lowers the melting-point and if the naphthalene has not been carefully centrifugalled to remove the maximum amount of oil and a high temperature is employed during the pressing, then an excessive quantity of naphthalene will come away with the press drainings. It is advisable to let the works chemist determine the best temperature at which to press any individual working of naphthalene.

In order to avoid the use of a number of salting-out tanks and to speed up the process of separating naphthalene from coal tar distillates, an apparatus has been patented[1] which consists of a series of horizontal cylindrical vessels, each being provided with an inner tube of steel in which is placed a rotating shaft fitted with a worm conveyor. The inner tubes of the series are connected by bends fitted with inspection doors, the arrangement being alternate at opposite ends of the apparatus. The jackets or outer vessels are connected in a similar manner by pipes. The method of procedure is as follows: Tar oil containing naphthalene is pumped into the first inner tube and passes through the series, whilst a fluid refrigerant is allowed to flow through the jackets in an opposite direction. It is not possible for the naphthalene which crystallises out to adhere to the walls of the inner tube owing to the motion of the worm conveyors, and therefore it is carried forward by the oil. The naphthalene is finally separated by means of centrifugal machines.

In the manufacture of the technically pure quality of naphthalene the crystals ("salts") from the salting-out tanks are melted and raised to a temperature suitable to allow transmission without choking the pipes, and charged into a still which is coal or gas fired. During distillation the water in the condenser is kept at a temperature between 85°–90° C. in order to prevent choking of the condenser coil. A small quantity of fore-runnings is removed (if a thermometer is fitted in the vapour pipe when this indicates a temperature of 210°–212° C.), and then the distillate is run as far as possible without endangering the still; some prefer to work until the thermometer indicates 230°–235° C. Topping may be practised if desired, or the bottoms from the still charge worked up with other bottoms later, or immediately run to salty creosote. The main distillate is allowed to cool and the naphthalene is then centrifugalised and finally hot pressed, or hot pressed only. The almost oil-free naphthalene cake is broken up, melted and washed, at a temperature of about 95° C., with three or four lots of sulphuric acid. Usually the total amount of sulphuric acid required will not exceed 3 to 3½ lbs. per 100 lbs. of naphthalene. The acid is allowed to drain away thoroughly after each washing, and following the last wash is one with water. During this wash the temperature may be raised to 100° C. to facilitate the separation of the wash water. In order to remove the last traces of sulphuric acid, about two washes with caustic soda solution of 35° Tw. (each approximating ¾ per cent. by weight of the naphthalene) are given and finally a water wash. If any difficulty presents itself in the way of separation at this point, the addition of a strong solution of sodium sulphate will clear it up. After the final wash the draining must be thorough in order to prevent any trouble during the process of redistillation. In this process the first runnings will be watery, and these are run to a receiver set aside for the purpose until the thermometer in the vapour pipe indicates a temperature of about 215° C., or better still, until the melting-point of a sample taken at the worm end is between 79·5°–79·6° C. When this point is reached the distillate is allowed to run into galvanised or tin-lined receivers, or similarly coated iron drums, until the temperature indicated by the thermometer is 220°–222° C., or the melting-point of a sample from the worm end shows signs of falling below 79·5° C.

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[1] Brotherton & Co., Ltd., J. Porteous and E. O. Whitelock, Leeds. Eng. Pat. 115,906, May 24th, 1917.

The process just described may be modified according to the source or condition of the naphthalene salts, and it is very advisable to remove all the tar acids from oils which are to be worked for their naphthalene. If tar acids are suspected in crude naphthalene salts intended for the manufacture of technically pure naphthalene, then it is advisable to give the melted salts a preliminary wash with caustic soda, and then with water, before commencing the acid washing. It is preferred by some to conduct the acid and first water washes in one washer, and after draining to continue the caustic soda and final water washes in another washer.

R. Kutschenreuter[1] proposes to purify naphthalene by recrystallising it from tetrahydronaphthalene. At 30° C. naphthalene is miscible in all proportions in this substance, whilst at 10° C. its solubility is 10 in 100, and below 6° C. it is practically insoluble.

According to The Barrett Co.[2] crude naphthalene may be purified by raising it to a temperature of about 85° C. with a quantity of water or other immiscible liquid and then agitating until an intimate mixture is obtained. When this condition is reached the mixture is allowed to cool gradually, agitating slowly all the time, until a temperature of about 65° C. is reached. The mixture is then submitted to a filtering process which removes the water and oily impurities.

Thionaphthene C_8H_6S occurs along with naphthalene, and in many ways its behaviour is very similar. Owing to the difficulty in removing it, technically pure naphthalene will contain traces. This substance can be obtained from crude naphthalene by treatment with sodamide at 120° C., extracting the resulting product thoroughly with benzene and then stirring it with ice-water which liberates the thionaphthene.[1]

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[1] Ger. Pat. 317,634, August 14th, 1918.

[2] Eng. Pat. 172,937, November 11th, 1921.

Attempts have been made to utilise naphthalene as a motor fuel, but it appears that up to the present efforts in this direction have not met with any great success (see *Gas Journal*, 1918, No. 1, 65–67).

According to Franz Fischer and Hermann Niggemann[2], if naphthalene is heated for one hour with 1 per cent. of iodine, at a temperature of 550° C., in an atmosphere of hydrogen, and at a pressure of about 170 atmospheres, it is converted into an oil possessing a blue fluorescence. After a few days this oil solidifies more or less completely, this action being due, it is thought, to oxidation and separation of dissolved naphthalene.

Attempts to produce liquid hydrocarbons from naphthalene suitable for use in the manufacture of lubricants have been made, but with what success, commercially, it is not known definitely. F. Fischer[3] heated naphthalene with aluminium chloride at comparatively low temperatures in an autoclave at a pressure of about two atmospheres, and then submitted the reaction mixture to steam distillation, and finally hot filtration through cloth. He obtained a black, syrupy residue, which on blending with three-parts of a tar lubricating oil, yielded a viscous liquid of high lubricating value. The reader is also referred to German Patent 299,134, 23.4.16, F. Fischer,[4] and to a paper by F. Fischer, W. Schrader, and S. Hilpert, in the *Gesellschaft Abhandlung zur Kenntnis der Kohle*, 1917, 1, 237–244.[5]

In order to discover a simple and technical method of converting naphthalene into liquid products, Franz Fischer and Wilhelm Schneider[6] experimented with ethyl and methyl alcohols as the source of the alkyl group. A reddish brown oil exhibiting a green fluorescence was obtained when 5 grams of naphthalene were heated under pressure for thirty-six hours with 4·5 c.c. of absolute alcohol in the presence of 10 grams of zinc chloride, the temperature varying between 290° and 300° C. The yield of oil amounted to 5·1 grams, and 0·2 gram of naphthalene was recovered. In another experiment 100 grams of crude naphthalene were heated under pressure (temperature 180°–190° C.) for sixty hours, with 120 c.c. of 96 per cent. alcohol and 400 grams of zinc chloride (made up of 200 grams of fresh and 200 grams of regenerated zinc chloride). The yield amounted to 112 grams of a dark brown crude oil with a green fluorescence, and on distillation this oil yielded a small fraction boiling below 240° C., 98 grams of a volatile yellow oil, boiling between 240° and 300° C., and 12 grams of a dark brown viscous oil as a residue. On chilling these fractions with ice-water naphthalene did not separate. An experiment in which methyl alcohol was used resulted in a somewhat lower yield, and one in which phenol was employed was quite unsuccessful as it yielded a considerable amount of carbon and large quantities of unchanged substances.

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[1] R. Weissgerber and O. Kruber, *Ber.*, 1920, 53 (B), 1551–1565.

[2] *Chem. Zentr.*, 1919, 11, 585–586. See also *J.C.S.*, 116, 1, 393.

[3] *Ges. Abhandl. zur Kenntnis der Kohle*, 1917, 1, 254. See also *J.S.C.I.*, August 15th, 1919, p. 528A.

[4] See also *J.S.C.I.*, October 15th, 1920, p. 653A.

[5] See also *Chem. Zentr.*, 1919, 90, 11, 584, and *J.S.C.I.*, August 15th, 1919, p. 528A.

[6] *Chem. Zentr.*, 1919, 11, 585. See also *J.C.S.*, 116, 1, 393.

Naphthalene can be hydrogenated with the production of mixtures of hydronaphthalenes by heating it under pressure in the presence of hydrogen and a metallic catalyst. The processes by which these products are obtained are covered by patents, chiefly German. The mixtures referred to contain chiefly di- and tetrahydronaphthalenes, but one patentee[1] states that by heating naphthalene at 180° C., under a pressure of fifteen atmospheres in the presence of hydrogen and metallic nickel (produced by reducing nickel formate dissolved in a saturated glyceride, by hydrogen) decahydronapthalene is obtained. According to Dr. Stanley Smith[2] this substance, called by him " Dekaline," is an excellent substitute for turpentine. It has a specific gravity of 0·900, a distilling point of 190° C. and flashes at 60° C., whilst its odour is aromatic, resembling somewhat that of camphor. In addition to the many varied uses it can be put to as a solvent, and as a cleansing fluid, it is claimed that it can be used as a substitute for petrol for oil engines and also as an illuminant if burned in ordinary paraffin lamps.

Further interesting and useful information on " Dekaline " will be found in an article by J. B. Coleman and P. Bilham.[3]

Naphthalene is oxidised to phthalic acid or phthalic anhydride by atmospheric oxygen in the presence of vanadyl chloride.[4]

According to C. Conover and H. D. Gibbs[5] naphthalene can be oxidised direct to phthalic anhydride if its (naphthalene) vapour is mixed with air and passed through a heated tube in the presence of vanadium pentoxide. This catalyst is fused and then finely powdered before using, and it seems to give better results than other known catalysts. As much as 61 per cent. of the naphthalene taken undergoes conversion under the most favourable conditions. There are several by-products of the reaction, and among those identified are benzoic acid, the naphthols, and carbon dioxide.

Naphthalene is decomposed when exposed to the action of canal rays, so are benzene, anthracene, and other hydrocarbon bodies. The substances formed vary in properties according to the amount of the potential at the cathode, and not in the manner of union of the carbon atoms in the material under treatment. Low potentials yield deposits which are transparent and coherent, and which when heated evolve large quantities of gas and tar, whilst high potentials produce practically pure carbon, having an appearance very much like anthracite.[1]

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[1] K. Wimmer, Ger. Pat. 300,052, March 14th, 1915.

[2] " Decahydronaphthalene, a new Solvent," *Chem. Trade Jour. and Chem. Eng.*, August 21st, 1920, p. 253.

[3] " The Properties and Composition of Dekalin," *Chem. Age*, October 21st, 1922, pp. 554–555.

[4] Eng. Pat. 164,785, British Dyestuffs Cpn., Ltd., A. G. Green and J. W. Porter.

[5] Contribution No. 53 from the Colour Laboratory of the Bureau of Chemistry, U.S.A., see also *Jour. Ind. and Eng. Chem.*, February, 1922, and *Chem. Trade Jour. and Chem. Eng.*, June 9th, 1922, 685–687.

Naphthalene is less toxic than benzene, but when poisonous doses are taken disturbances of the alimentary canal and/or the kidneys are produced. The rate of respiration is often lowered, and it also decreases nitrogen metabolism.

In the preparation of crude anthracene, if it is desired to redistil the anthracene oil as obtained direct from coal tar, then a quantity of this is charged into a still, and the fraction which comes over between the point at which the distillate tests 14° Tw. at 60° F. and that at which it tests 26° Tw. at 60° F., or when it shows what is termed "grease," collected for this purpose. These figures are only approximate, and have to be varied according to the nature of the oil under treatment. It is rather difficult to explain what is meant by "grease." The distiller, by experience, is enabled to tell from the appearance of the distillate, if a small portion is allowed to cool on a piece of iron or glass plate, when anthracene approximately ceases and higher solid bodies appear. The presence of anthracene in the oil is generally shown by a curdy or gritty appearance when the oil is chilled, and "grease" when the oil on cooling sets to a buttery-like mess. The anthracene fraction is pumped into the crystallising tanks situated in the press house, and there allowed to cool in order to separate out the crude anthracene.

Should it be desired to deal with the anthracene oil fraction as obtained from the tar stills, this is pumped from the receiver into the crystallising tanks, and is submitted to the same process as the redistilled "green oil" fraction. The length of time which the contents of the crystallising tanks have to rest in order to complete crystallisation will vary according to the time of the year, unless the chamber or the tanks are artificially cooled. From two to five days may be taken as averages throughout the year.

After the separation of the crude anthracene has taken place the contents of the tanks are pumped through filter presses, or else into bag filters, which are prepared by tying special bagging over flanges fitted into the pumping main, and then fastening up the bottoms with cord, the lot being suspended over a tank to catch the drainings; or else into an ordinary filter tank across which is suspended a filter bed made of filter cloth or bagging, and supported by wicker or basket ware. At the present day the filter press is generally used, as it deals with the material most expeditiously. In pumping through a filter press, the pressure must be raised gradually and kept as long as possible at a low point. When the press is full and oil ceases to run from the press plates the press is opened and the cakes of filtered anthracene are removed. The filtrate, whichever way obtained, is known in the trade as strained or dead oil. The cakes from the filter press may be submitted to pressure in a hydraulic press, and then ground up and washed, or else washed first, and after a further filtering pressed by hydraulic pressure, according to the quality of crude anthracene it is desired to produce. If it is required to press first, the cakes are broken up and charged into bags and then into the press, and then submitted to hydraulic pressure in a similar manner to that described under naphthalene. Sometimes the crude anthracene from the filter is passed through a centrifugal machine before submitting to hydraulic pressure. The filtered material is filled into bags, and these are packed into the cage of the centrifugal, or if a suitable gauze is fitted to the cage, the crude anthracene may be charged into it direct. Often hydraulic pressure is applied at an elevated temperature. This is carried out by employing a steam-heated hydraulic press.

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[1] V. Kohlschütter and A. Frumkin, *Ber.*, 1921, 54, 587–594. See also *J.S.C.I.*, 1921, 340A.

After the pressing operation is completed, the cakes are removed from the bags, ground under an edge-runner, or better, reduced to a fine state of division in a disintegrator, charged into the washer and washed with " salted out " (liquid) light creosote or a moderately heavy naphtha free from naphthalene, followed by two washes with pyridine bases. The quantity of liquid used for each wash of one ton of pressed anthracene is about 500 to 600 gallons. When the washer is charged, the contents are heated up by the aid of closed steam and thoroughly well agitated. While washing a temperature of about 80° C. is maintained, and the period of agitation varies according to individual ideas, but averages about three hours. After the washing operation, the contents of the washer are allowed to cool down to about 20° C. and then pumped through a filter press, the press cakes removed, and either hydraulically pressed, ground up, and spread out to dry in a drying room, or else roughly broken up as removed from the filter press and dried. The more complete the separation of the washing liquid from the crude anthracene, the purer the product ; so if circumstances allow, it is far better to hydraulically press after the filter pressing operation than to dry after removing from the filter press. Some manufacturers prefer to use a centrifugal machine in place of a hydraulic press. A point worth bearing in mind is that the same kind of oil should be used for the washing of all batches of anthracene, should it be desired to produce the same quality of this material.

A high percentage anthracene may be obtained[1] by dissolving crude anthracene in hot phenol, cresol or xylenol, or mixtures of these substances and then allowing the solution to cool, separating the crystals which deposit by filtration, and washing them with benzene, or with an aqueous alkaline solution, and then with water, repeating the treatment if necessary, and finally purifying the anthracene by crystallisation from pyridine bases.

B. Hardman publishes evidence[2] that anthracene of over 90 per cent. purity can be obtained by the use of a combination of Wirth's nitrous acid process[3] and a recrystallisation from heavy pyridine bases. The procedure is briefly as follows : To every 100 parts of crude anthracene (containing, say, 38·2 per cent. of anthracene) mixed with 150 parts of solvent naphtha (90 per cent. at 160° C.), diluted R.O.V. is added in sufficient quantity to decompose ten or more parts of sodium nitrite. This salt is dissolved to a 10 per cent. solution and added to the mixture at the ordinary temperature, whilst being agitated, at such a rate that red fumes do not escape. The agitation is continued for some time after the whole of the nitrite solution has been added. The mixture is then filtered on a vacuum filter, and the residue well washed with solvent naphtha. This naphtha can be used for the next charge of anthracene. The first filtrate consists of a mixture of solvent naphtha containing impurities washed out of the anthracene, and a dilute solution of sodium sulphate. Separation is allowed to take place, the sodium sulphate liquor run to waste and the solvent naphtha freed from its impurities by distillation. One result obtained by this part of the combined process, taken from a table showing many, is given below :—

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[1] Eng. Pat. 119,855, July 23rd, 1918. Soc. d'Eclairage Chauffage, et Force Motrice, Paris.

[2] *Chem. Trade Jour. and Chem. Eng.*, July 23rd, 1921, p. 94.

[3] Ger. Pat. 122,822, and Fr. Pat. 302,998.

No.	Anthracene taken, grams.	Purity, per cent.	$Na\,NO_2$ used, grams.	Duration of experiment, minutes.	Yield. grams.	Purity. per cent.	Efficiency of recovery, per cent.
8	1000	38·2	120	270	425	8·10	90·20

The nitroso-purified anthracene is then dissolved in hot, heavy bases, cooled to 30° C., filtered on a vacuum filter and then washed on the filter with more heavy bases, and finally dried. In an experiment using an anthracene testing 81 per cent. pure, obtained by the nitrous acid method detailed above, 380 grams were taken and dissolved in 600 c.c. of hot, heavy bases previously used for washing. The solution was cooled to 30° C., filtered, and the anthracene on the filter washed with 600 c.c. of clean, heavy bases, after which it was dried. The resulting anthracene, 320 grams, tested 94·8 per cent. pure.

This combination process is certainly worth consideration, and the reader is referred to the original paper for full details.

According to Eng. Pat. 144,648, 7.6.20.,[1] carbazole can be separated from crude anthracene by dissolving the anthracene in boiling solvent naphtha (b. pt. 145° C.) and agitating with potassium hydrate until water ceases to distil over. If necessary additional quantities of solvent naphtha are added to the reaction mixture. Finally, the sandy precipitate of potassium-carbazole is separated from the boiling solution, and the pure anthracene recovered by allowing the solution to cool.

A method of recovering anthracene, carbazole, and phenanthrene from anthracene oil is given by J. M. Clark.[2] Anthracene oil is cooled, the oil drained off and the crude anthracene centrifuged or pressed. Ten thousand grams of a typical sample of oil-free crude anthracene, containing 30·1 per cent. of anthracene, 22·0 per cent. of carbazole, and 47·9 per cent. of phenanthrene, was mixed with 15,000 grams of crude coal-tar naphtha and slowly heated to 80° C. The mixture was then cooled to 30° C., and filtered. The insoluble portion (A) weighed 4,125 grams and consisted of a mixture of 60·2 per cent. of anthracene, 35·1 per cent. of carbazole, and 4·7 per cent. of phenanthrene. The soluble portion (B) on distilling off the naphtha yielded 5,760 grams of a mixture of 8·4 per cent. of anthracene, 11·1 per cent. of carbazole, and 80·5 per cent. of phenanthrene. To the insoluble portion (A) was added 10,000 grams of light pyridine, and the mixture slowly heated to 80° C. It was then cooled to 15° C. and filtered. The insoluble portion (C) consisted of a mixture of 85·2 per cent. anthracene, 13·6 per cent. carbazole, and 1·2 per cent. of phenanthrene, and the soluble in the light pyridine (D) was composed of anthracene, 16·4 per cent.; carbazole, 72·2 per cent., and phenanthrene 11·4 per cent. Purification of the insoluble portion (C) was carried out by a further treatment with pyridine, then sublimation, a distillation after fusion with potassium and sodium hydroxides, and crystallisation from benzene, yielding 645 grams of a product containing anthracene 99·91 per cent., carbazole 0·06 per cent., and phenanthrene 0·03 per cent. The portion soluble in light pyridine (D), after separation, was treated with naphtha as before, and yielded 1,241 grams of material containing 81·5 per cent. of carbazole. Purification of this material was effected by treatment with 98 per cent. sulphuric acid and then the addition of water, which dissolved the sulphonated anthracene. On subliming the insoluble portion 960 grams of carbazole, testing 99·5 per cent., was obtained. The soluble portion from (B), 5,760 grams, was again treated with naphtha and fractionated into an insoluble portion (825 grams) containing 2·8 per cent. of phenanthrene, and a soluble portion, which, after the separation of the naphtha, yielded 4,872 grams of a product containing 93·8 per cent. of phenanthrene. By fusing this material with sodium and potassium hydroxides, then distilling, giving a further treatment with naphtha, decolorising with bone black, and treating with alcohol, 2,490 grams of pure crystallised phenanthrene was obtained.

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[1] Kinzlberger & Co.

[2] *Jour. Ind. Eng. Chem.*, 1919, 11, 204–209. See also *J.S.C.I.*, April 30th, 1919, p. 247A.

It was found that a large excess of sulphuric acid is required to remove anthracene from carbazole, and for the removal of carbazole from anthracene or phenanthrene, fusion with sodium and potassium hydroxides gave the best result.

Vesely and Votocek[1] purified crude anthracene by dissolving it in a solvent which is immixible with sulphuric acid, raising the temperature, and then agitating with concentrated sulphuric acid. The temperature and agitation are maintained for several minutes, a short time for settling allowed, and the sulphuric acid containing the impurities then separated. In order to free the anthracene solution from traces of acid, the required quantity of calcium carbonate is added with agitation. The whole mixture which is still hot is then filtered, and the anthracene recovered by crystallising from the solvent. The proportions used in the process are: Crude anthracene 100 parts, solvent naphtha 300 parts, and sulphuric acid 100 parts.

It is stated that the best method of purifying crude anthracene is to wash it with pyridine or quinoline bases.[2] A crude material treated with one or other of these solvents will yield a product containing between 90 and 98 per cent. of pure anthracene.

Crude anthracene obtained from paraffinoid tars is not sought after by alizarin manufacturers, owing to its comparatively high paraffin content; the presence of paraffin bodies causes trouble during filtering operations.

Attention is called to the fact that workers with anthracene and anthracene oil are liable to contract epitheliomatous cancer if due care is not taken.

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[1] Ger. Pat. 164,508; Eng. Pat. 27,596, 1904.

[2] D.R.P. (Ger. Pat.) 42,053 of Chemische Fabriks-Actiengesellschaft in Hamburg.

Block and Dreyfus[1] consider that the active substance which affects workers in the tar distilling and kindred industries, producing epitheliomatous cancer, is contained in the anthracene fraction of coal tar, which boils above 300° C. Dr. Murray[1] has obtained an extremely active extract from coal tar by submitting it to successive extractions with water, alcohol and ether. See also Chapter XIX, page 333.

Carbazole. During the last few years carbazole has attained to some importance, owing to the fact that a number of its derivatives can be used as vat colours. These colours are very fast to chlorine and to light.

As already stated carbazole occurs in fair quantity in crude anthracene, and is recovered from by-products obtained in the process of purification of this material. If the anthracene is purified by washing with pyridine bases, then the carbazole can be recovered from the material deposited when the bases are removed by distillation, or if caustic potash was used in the anthracene refining process, then the potassium-carbazole formed, will, on dilution with water, yield carbazole. Also, this substance can be recovered from concentrated sulphuric acid if this is used to refine anthracene.

According to Brit. Pat. 139,441, 1919,[2] carbazole can be purified and obtained in well-defined crystals by slowly diluting with water its solution in concentrated sulphuric acid. The process of dilution may be affected by exposing the solution to a moist gas or to a damp atmosphere, with or without agitation, or as an alternative by blowing through the solution moist air or a moist gas. If desired the solution may be first diluted rapidly to a point approaching that at which precipitation takes place and then diluting slowly as just described.

Burt, Boulton, and Haywood, and F. D. Miles[3] isolate carbazole from mixtures containing it by converting the carbazole into an alkali-carbazole. The alkali salt is prepared by treating the raw material with the oxide or hydroxide of the alkali metal or with the alkali metal itself in the presence of a neutral solvent, and at a temperature below the melting-point of the alkali-carbazole. The process may be carried out at the ordinary atmospheric pressure or under elevated pressures, the solvent varying according to the pressure chosen. As examples, naphthalene is given as a solvent which can be employed at ordinary atmospheric pressures, and toluene for higher pressures.

For the production of high percentage carbazole the following process has been patented.[4] Crude carbazole is dissolved, at about 70° C., in commercial carbolic acid, the cresols or the xylenols, using 5 to 10 parts of the chosen solvent according to the richness of the carbazole. The hot solution is filtered, and the filtrate allowed to cool, and the crystals which separate washed with a small amount of the solvent used at first. The product from this crystallisation will yield a carbazole testing 80 per cent., and this may be purified to a 90 per cent. carbazole by a second crystallisation from any of the solvents mentioned above. The crude carbazole employed as the initial material may be that obtained by the action of water on potassium-carbazole, or the residue resulting from the distillation of pyridine bases used in the purification of anthracene.

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[1] (Report of the 19th Annual Meeting of the British Medical Association), *British Medical Journal*, December 9th, 1922.

[2] South Metropolitan Gas Company and W. Kirby, London.

[3] Brit. Pat. 139,981, 1919.

[4] Eng. Pat. 121,455, October 7th, 1918. Soc. d'Eclairage, Chauffage et Force Motrice, Paris.

At the present time the uses for phenanthrene are not large. It has been employed to a certain extent in the coal tar dyestuffs industry, and at least one synthetic alkaloid of the morphine group, "epiosine," has been prepared from it. In the near future it is quite possible that further investigations will develop the uses of phenanthrene in the two industries just mentioned and also in others.

As already described on page 327, phenanthrene can be readily recovered from the solvent naphtha used in the process of preparing high percentage anthracene from the crude material.

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CHAPTER XIX

PITCH AND PITCH "GETTING"

Coal tar pitch is a complex mixture of hydrocarbons, basic and non-basic nitrogen compounds and oxygenated compounds, all of high boiling-point, and "free carbon." It is not completely soluble in any one of the usual solvents, the amount going into solution varying according to the solvent used. Phenols and pyridine bases are among the best solvents, but whether these are used or the less vigorous ones, "free carbon" always separates. In almost every case the solvent appears to exert a selective action, and this fact has caused a good deal of discordance in regard to the results obtained by the several methods of estimating "free carbon" in pitch.

There are three chief grades of pitch, viz.: soft, medium, and hard. These grades are distinguished from one another by what is known as their "twisting" or softening point. This point will vary somewhat according to the method used to obtain it: for soft pitch the average is about 110° F., for medium pitch 140° F., and for hard pitch 210° F. At the present day a very large quantity of pitch is purchased on the amount of volatile matter which it contains. The methods of conducting these tests are fully described in Chapter XXII.

With reference to soft pitch, this is not made in very large quantities, and when it is it is generally filled into barrels, when sufficiently cool, instead of running on to a bay. It is a matter of impossibility to dig or "get" this pitch during the summer months. By far the largest quantity of pitch made is of the medium hard quality, and this, or the grade known as hard pitch, is run from the pitch coolers on to the bay, which is prepared as described in Chapter IX, page 187. It is advisable not to run the pitch to too great a depth, the best thickness being between 15 inches to 18 inches. This depth of pitch will cool rapidly, and is dug with a minimum of labour by the pitch-getters. With reference to the length of time that the pitch must remain on the bay before it can be "got," this will vary, naturally, according to the temperature of the atmosphere and the situation of the pitch bay. Under favourable conditions 24 to 36 hours is all that is necessary, but there are times when two or four days must elapse before pitch can be dug.

During the summer months it is advisable to "get" the pitch at night, or in the early hours of the morning, rather than during the hottest part of the day; and in order to keep the pitch cool, especially that portion which cannot be worked immediately, the surface should be covered with a thin layer of lime wash. This will prevent the absorption of the sun's rays during the daytime. If it is necessary for the men to work pitch which has been lime-washed on the surface, during the daytime, especially while the sun is shining upon it, the portion on which they are working should be washed with water and a hard brush to remove the lime-wash, as otherwise the glare will injure the men's eyes.

It is a general practice among pitch-getters, in order to protect the eyes, to wear a piece of black crêpe over them. This is not an efficient method of protecting these organs, as sometimes rather large particles of pitch will fly up from the bed, and will easily damage the eye in spite of the crêpe. Goggles made of fine copper wire gauze of between 30 to 40 meshes to the inch are much more suitable for this purpose, as the gauze will offer a considerable amount of resistance to flying pieces of pitch. It should be added that the workmen do not care about wearing goggles, and in many cases will not even wear crêpe. However, the management should insist upon this means of protection as a precaution against claims under the Workmen's Compensation Act. A good plan in order to prevent excessive rising of dust is to wet the pitch at the point where it is being dug, and often the workmen will carry this precaution out without being told.

Pitch is " got " by driving metal wedges into the layer on the bay with sledge-hammers weighing about 10 to 14 lbs. This breaks off large pieces, which are further reduced by the aid of pickaxes. The pitch is then shovelled into barrows or iron skips, according to the situation of the bed or the manner adopted by the management for loading trucks or carts. Sometimes the pitch bay is so situated that carts can be backed into it, and loaded direct by throwing the pitch into them with a shovel. If the bay is below the ground level, then it is necessary either to wheel the pitch in barrows up barrow-runs, or else to raise it in skips by means of a crane. If the pitch bay is above the level of the railway trucks, then it is quite a simple matter to wheel the pitch in barrows from the point where it is being " got " and tip it into the trucks at the end of the run.

With reference to wedges, these must be made of good steel, about 2 feet 6 inches long and $1\frac{1}{2}$ inches by $1\frac{1}{2}$ inches in section ; " set temper " steel is a very suitable grade to use. New wedges should be tough, but not brittle, as the tendency seems to be for the steel to become very brittle in time, owing to repeated hammering and to the presence of fine pitch dust, which settles upon the head of the wedge. Brittle wedges are dangerous, as particles fly off and often cause accidents by cutting the " getter " about the body. The same remark applies to the hammers. Sledge-hammers having two faces are the best type to use, and the average workman prefers one of about 10 lbs. in weight.

According to T. Howard Butler[1] one of the most successful modern methods of dealing with coal tar pitch is to allow it, while hot, to run into pans holding approximately half a ton. When the pitch is cold the pans are picked up by a crane and swung over a railway truck and then tipped, the whole block of pitch falling into the truck at this operation. By the use of this method the pitch is not handled by the workmen, and the only objection to it being a large capital outlay on pans, light railways, cranes, etc.

The cost of " getting " pitch and loading it into wagons will vary somewhat for each works, according to the position of the pitch bay, the thickness of the pitch on the bay, the time of the year, and so on. Under normal conditions in a properly arranged and well-managed works it will vary between 6d. and 7½d. per ton, including repairs. The average cost of repairs should work out at ¼d. per ton.

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[1] " Modern Practices in Coal Tar Distillation," *J.S.C.I.*, January 31st, 1918, p. 23T.

These are pre-war figures, and to bring them into line with present-day costs additions must be made according to the percentage increase of raw materials, labour, etc.

For many years it has been known that certain men engaged in the handling of pitch (and also anthracene) develop warty growths. These growths often ulcerate, and at times render it necessary to remove, by surgical treatment, the affected part. A year or two back a special inquiry was made at the instigation of the Home Office into this question, and it was discovered that these ulcerated warty growths occasionally become the seat of what is termed by medical men epitheliomatous cancer. This form of cancer is considered to be the least malignant, and if removed is not usually followed by a recurrence. Draft regulations were drawn up, and in the course of time objections were raised against these. Among the draft regulations, it was suggested that bathing and washing on the factory premises should be carried out. It was required that the workmen should take a bath at the works at least every alternate weekday, and wash before leaving the works for meals, or at the end of the day, when a bath is not taken. One of the chief objections raised against these regulations was that of washing and bathing, the workmen stating that the application of water to the skin after pitch-getting caused them a considerable amount of pain. Owing to this and other objections a Home Office inquiry was made to consider the same, and an interesting pamphlet was published dealing with the results of the inquiry.[1]

It appears that pitch dust also causes severe inflammation of the conjunctival membrane and cornea of the eye, and in some cases may result in the formation of epithelimatous cancer on these membranes. In any case there is great danger of septic inflammation being set up, owing to bacteria getting into the ulceration, and the possible chance of the loss of sight. The wearing of goggles or crêpe will not prevent the fine pitch dust from getting into the eyes, and on this account it is advisable to wet the pitch somewhat at the point of working, as already stated, in order to prevent as far as possible the rising of dust during the "getting" operation.

The pamphlet just mentioned does not state what is the actual cause of the irritation, although it seems to point to the fact that the cause is two or more of several chemical substances contained in the pitch (or crude anthracene). These substances are divided into two groups : the *auxetics* (excitors of reproduction) which stimulate cell multiplication and *kinetics* (or augmentors) which increase the action of the auxetics. It appears that pitch cancer cannot be produced unless an auxetic and a kinetic are present. The auxetics appear to be bodies akin to the amido acids or their derivatives and the amines, and the kinetics substances of the ptomaine class, such as cadaverine and choline.

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[1] *The Problem of the Gas Works Pitch Industries and Cancer.* John Murray, Albemarle Street, London, W.1.

The author made some experiments a while ago and was able to isolate small quantities of acridene from coal tar pitch, and, on making a few experiments with this material, found that it set up considerable irritation, particularly when applied to mucous membrane and especially when wetted. Possibly acridene is one of the hurtful substances of the auxetic type, but it rests with the medical men carrying out the inquiry to settle such a matter as this.

According to H. C. Ross and J. W. Cropper[1] if the distillation of a gas works tar is finished at 360° C. the pitch obtained therefrom will not produce epitheliomatous cancer. These workers also find that pitch from blast-furnace tar is quite innocuous in this respect. Dr. J. A. Murray[1] points out that in tar stillmen and pitch workers the interval between the first contact with tar or pitch and the appearance of malignant disease is never less than ten years and may possibly extend to thirty or forty years. See also Chapter XVIII, page 329.

It is said that pitch disease (epitheliomatous cancer) is absent in those briquetting factories in which the pitch is used in a fluid condition.[2] The reason for this is, no doubt, due to the absence of pitch dust and the non-handling of the pitch by the workmen ; soft pitch as well as hard pitch contains the auxetic and kinetic bodies which are necessary to produce epitheliomatous cancer. The soft pitch is made fluid by the addition of about 20 per cent. of tar and then atomised by means of air and steam, the jet being so arranged that the spray of pitch mixes with the fine coal, etc., in a rotating chamber. (Fohr–Kleinschmidt–briquetting process.)

Several methods have been suggested for the removal from coal tar of the substances which induce cancer, and among them are those of H. W. Robinson and H. C. Ross.

Robinson's methods are briefly as follows : British Patents 4,159 and 10,156, February 8th and April 30th, 1913. The addition of small quantities of formaldehyde or other aldehyde to coal tar at a suitable stage in the distillation process results in a pitch entirely or almost free from auxetics and, therefore, harmless as regards liability to induce pitch cancer. Sugar or other substance which decomposes at a temperature below 250° C. with the formation of an aldehyde may be used. If formaldehyde is used it is added along with the steam after removing from the tar all the fractions which come over before anthracene oil. The quantity recommended is 1½ gallons of 40 per cent. formaldehyde for each 2,000 gallons of tar.

Robinson : British Patent 20,767, September 15th, 1913. Tar is treated for 60 to 90 minutes with ozonised air applied at a pressure of 20 to 30 lbs. per square inch.

Ross suggests the following : British Patent 11,984, March 22nd, 1913. The auxetics in tar are removed by bringing the tar into intimate contact and spraying it with hot water or hot dilute acid. The mixture is projected on to a plate or plates to bring about a finely divided state, after which it is allowed to stand to separate the aqueous liquid or is treated by any other suitable process to attain this end.

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[1] *British Medical Journal*, December 9th, 1922. (Report of the 19th Annual Meeting of the British Medical Association.)

[2] P. M. Grempe, *J. Gasbeleucht.*, 1919, 62, 243–244.

If hot water at a temperature between 100° to 212° F. is employed then a volume twice that of the tar is taken, and if dilute acid is used, a volume one-half that of the tar will suffice. Sulphuric or hydrochloric acid of 5 per cent. strength is recommended.

Up to the time of writing there seems to be an absence of details as to whether any of the above processes have produced satisfactory results.

In the manufacture of patent fuel (coal briquettes) coal tar pitch is almost exclusively used both at home and abroad as the binder. There are several important points to observe in choosing a suitable pitch for briquette making, and among these are the amount of volatile matter which the pitch contains, the amount of "free carbon," and the quantity of material soluble in carbon disulphide. Although excessive amounts of "free carbon" are deleterious in effect, the average pitch manufactured in this country will not contain sufficient to cause trouble. The carbon disulphide test is one of many which determines this so-called "free carbon," and it is perhaps wise for the seller of pitch for briquette making to obtain from his buyer the method by which he would like the "free carbon" determined. For details of some of these methods, the reader is referred to page 378 in Chapter XXII, and also to the *Transactions of the Junior Gas Association*, Vol. 2, pp. 106–109.

Satisfactory pitches should not contain more than 30 per cent. of "free carbon."

In regard to the determination of the volatile matter, reference should be made to page 388, Chapter XXII, and also to the *Transactions of the Junior Gas Association*, Vol. 2, pp. 113–116.

The coke which is left in the crucible after the volatile matter has been driven off, should be examined carefully; those pitches which yield a swollen coke must be considered as unsatisfactory, a satisfactory pitch producing a flat button of coke of a very dark greyish colour. This residual coke can be used for a determination of the ash content which must not exceed 1 per cent.

The softening point of pitch, suitable for briquette making, is approximately 140° F.

In addition to the manufacture of patent fuels, pitch also finds application in the preparation of cellulose fibre compositions, and it is necessary that the pitch which is to be used for this purpose must be in a very finely divided state. Fred. J. Commin[1] reduces pitch to an extremely fine state of division by grinding it in the presence of a solution of a peptising agent. Suitable peptising agents are, a solution of sodium rosinate in water, or a solution of casein in a dilute solution of alkali.

Pitch can be used as a fuel if it is first melted and then atomised, by means of a specially designed jet, into the furnace.[2]

Another use for coal tar pitch is in the manufacture of various types of black varnish. These are made by melting the pitch and adding carefully varying quantities of heavy and light coal tar oils, according to the quality of black varnish desired.

Coal tar pitch also finds an outlet in the manufacture of the cheaper types of insulating compositions, such as cable troughing, and it enters into the composition of a gunpowder known as " Petroklastit " (Haloklastit).

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[1] Eng. Pat. 162,727, January 2nd, 1920.

[2] Eng. Pat. 118,890, September 14th, 1917.

At times coal tar pitch is subjected to the coking process in order to obtain heavy oils and chiefly a coke for use in the manufacture of arc lamp carbons. According to A. Fischer,[1] cast-iron retorts of a diameter between 1·5 and 2·5 metres are best in which to coke coal tar pitch. The exit pipe leading from the retorts should be not less than 20 cm. in diameter, and a full setting of these retorts is either five or ten. As a rule the retorts are fired by coal, and this is assisted at the end of the operation by superheated steam. It takes approximately 24 to 36 hours to complete a distillation and of this time about three hours are required to bring the retort contents up to the temperature at which distillation commences. Care must be taken during the preliminary heating, especially if the pitch has a low carbon content, as " foaming " is likely to take place. At the outset of the operation light oils distil over containing a trace of water. The temperature then rises to approximately 300° C., when the distillate consists of a thick brown fluorescent oil possessing a specific gravity of 1·15 to 1·17 ; accompanying this distillate are ammonia and non-condensable gases. Between the temperatures of 375° and 380° C. a small quantity of " resinous " material distils over. Average yields obtained by Fischer are :—

Oil : 40–50 per cent.
" Resinous " material : 4–6 per cent.
Coke : 50–60 per cent.

with small quantities of ammonia. The coke, in order to be satisfactory for the manufacture of arc lamp carbons, must not contain more than 0·5 per cent. of material soluble in benzole, and the amounts of fixed carbon should be between 98 and 99 per cent.

In connection with the distillation and carbonisation of coal tar pitch the reader is referred to English Patent 129,091 of 1918.[2]

According to H. Tindale[3] coal tar pitch can be separated into four constituent oils boiling up to 300° C., petrolenes, asphaltenes, and " free carbon." In vertical retort tars, asphaltenes are said to occur in amounts varying between 25 and 30 per cent., and in horizontal retort tars between 35 and 40 per cent. The patentee considers that the asphaltenes are the most desirable constituents in a road tar. If this contention is correct, then it is another addition to our knowledge of why prepared horizontal retort tars are much more useful as road tars than those prepared from vertical retort tars.

For the benefit of the student it should be mentioned that in the natural bitumens, such as Gilsonite, Trinidad bitumen, etc., petrolenes are soluble in acetone and asphaltenes are soluble in chloroform.

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[1] *J. Gasbeleucht.*, 1919, 62, 510–513. See *J.S.C.I.*, November 15th, 1919, p. 807A.

[2] F. M. Perkin and Nitrogen Products and Carbide Co., London.

[3] Eng. Pat. 163,199. See *J.S.C.I.*, 1921, 463A.

CHAPTER XX

CREOSOTE

The term creosote is used very broadly in the commercial world, and under it are often included oil-gas tar creosote, wood-tar creosote, coke-oven creosote, blast-furnace oil creosote, and several others. In this chapter it is intended to deal with coal-tar creosote only.

Owing to the facts that coal-tar creosote is a comparatively cheap article ; that its present commercial uses do not *appear* to warrant it ; and perhaps because from the viewpoint of the research chemist it is not an attractive substance to work upon, its composition has not been thoroughly investigated. It appears to consist chiefly of a mixture of moderately high to high-boiling hydrocarbons with smaller quantities of phenolic and basic substances.

Coal-tar creosote as put on the market varies within fairly wide limits as regards specific gravity, content of phenols and naphthalene and distilling range. The gravity may vary between 1·000 and 1·070. Occasionally samples are met with a little lower in gravity, and sometimes higher. With reference to the percentage of tar acids, creosotes are sold containing but a mere trace up to about 25 per cent., and with regard to the percentage of naphthalene, this varies very considerably, some creosotes containing 30 per cent. and even more, others but mere traces. Some idea of the variation in distilling range will be obtained by referring to Table 64.

TABLE 64

From drop to 200° C.	From drop to 250° C.	From drop to 300° C.	Residue.
Per cent. 0 to 16	Per cent. 25 to 75	Per cent. 63 to 85	Per cent. 5 to 35

Creosotes as obtained direct from coal tar by distillation differ somewhat according to the quality of the tar, and more often than not are put through a special treatment, *i.e.* removing a certain portion of the tar acids or naphthalene or submitting to a redistillation, before placing on the market. If the latter treatment is resorted to the virgin light creosote fraction, obtained during the distillation of coal tar between the points 5° Tw. and 11° Tw. at 60° F., is redistilled in a fire-heated still, two or three fractions being collected. These distillates will consist of :—

1. A crude naphtha fraction.
2. A light oil fraction, and
3. A redistilled creosote fraction.

Fractions 1 and 2 and sometimes fraction 3 are washed with caustic soda with the object of recovering the tar acids contained therein. Frequently, owing to the fact that most buyers require creosote to answer their own specification, blends of various grades have to be made. A creosote required for burning, say, in a Wells lamp must be quite free from dirt and naphthalene. As a matter of fact it should not deposit " salts " (or naphthalene) at a temperature of 40° F. after exposure to that temperature for six hours. The average specific gravity of creosote for this purpose is 1·050–1·060 at 60° F., and it should not contain more than 2 per cent. of water when tested by distillation.

Creosote oil, if properly prepared, makes a fairly good fuel oil when compared with petroleum fuel oils, such as American residuum, Russian ostatki, and shale oil. Much care must, however, be employed in the preparation, otherwise troubles will result when it comes to be burned. It is necessary to use a heavy creosote or, better still, an anthracene oil for fuel purposes, and it must be free from any kind of solid matter, such as that of an earthy, carbonaceous or fibrous nature, and according to some users from naphthalene or anthracene salts also. All these bodies will choke the orifices of the nozzles of the burners, and naphthalene or anthracene salts will also choke up the supply pipes in the cold weather, and at times form a crust round the mouths of the burners unless provision is made to prevent these undesirable occurrences. In many specifications it states that fuel oil must be liquid at 60° F., but it should be noted that " salty " creosote *can* be used as a fuel oil if it is kept at an elevated temperature in the supply tank and fed to the atomising burners through steam-jacketed pipes. It must be quite free from water, as the presence of this material will probably cause the flame to go out, and if this is not noticed a disastrous explosion may take place in the furnace, owing to the oil spray and air forming an explosive mixture. Not more than 0·5 per cent. of water, determined by distillation, should be allowed. The flash-point must not be low, the minimum being 150° F. Abel's close test. Creosote will, if properly prepared, test above 210° F. Abel's close test. Creosote fuel oil, if burned with care in regard to air supply, will give excellent results and smoke troubles need not be feared. The calorific power of this type of fuel oil varies more or less between 16,200 and 17,500 British thermal units per lb. For purposes of comparison the figures given in Table 65 will prove of use.

TABLE 65

Kind of Fuel Oil.	Specific Gravity.	Flash-point ° F.	Calorific value by bomb. per lb Calories.	Calorific value by bomb. per lb B.Th.U.	Actual evaporative power in practice from and at 212° F. lbs.
Heavy tar oil .	1·084	218	8,916	16,050	12·0
Blast-furnace oil .	0·979	206	8,933	16,080	12·0
American residuum	0·886	350	10,904	19,627	15·0
Russian ostatki .	0·956	308	10,800	19,440	14·8
Shale oil . .	0·875	288	10,120	18,217	13·8

Most of the heavy tar distillates are found to be suitable for Diesel engine fuel. H. Moore[1] states that tar oils of British origin possess a gross heat value which averages out 10·2 per cent. less than that of the usual type of petroleum oils sold for oil engine purposes, but the increase in consumption is not higher by this amount, because tar oil generally yields a higher thermal efficiency than petroleum oil. This is probably due to the tar oils possessing lower viscosities. Owing to the average hydrogen content of tar oil being only about 6·9 per cent. as against approximately 11·5 per cent. for petroleum oils, the difference between the gross and net calorific values is not so great for the former as with the latter. The trouble arising in obtaining ignition of tar oils is due chiefly to its high ignition point; this averages about 480° C. as against 260° C. for petroleum oils. On this account petroleum or shale oil is necessary as an ignition oil when using a normal tar oil. The combustion of tar oil is helped to a small extent by allowing the circulating water to reach comparatively high temperatures. It is not an advantage to mix the petroleum with the tar oil because, in order to get a moderately good result, approximately half petroleum has to be used. It is absolutely necessary that tar oils to be used for Diesel engines must not contain a large percentage of ash, and even small quantities of an abrasive ash will bring about trouble. Another cause of trouble in tar oils is traces of pitch, which almost invariably contain "free carbon."

The following specifications for creosote which is to be used as a fuel for Diesel oil engines will, no doubt, be of use to certain readers :—

1. Continental specification :—[2]

   Tar oils must not contain more than a trace of constituents insoluble in xylol.
   The water content should not exceed 1 per cent.
   The coke residue should not exceed 3 per cent.
   At least 60 per cent. of the oil should be distilled on heating up to 300° C. (572° F.).
   The net calorific value should not be less than 15,840 B.Th.U. per pound.
   The open flash must not be below 65° C. (143·6° F.).
   The oil must be quite fluid at 60° F.

2. Day's specification :—[3]

   The tar oil must be a product of the distillation of coal tar.
   No product that has not undergone distillation must be present.
      Insoluble in xylol, not more than 2·00 per cent.
      Ash, not more than 0·08 per cent.
      Water, not more than 2·50 per cent.
      Coking residue, not more than 3·00 per cent.
   The oil must be liquid at 60° F. when maintained at that temperature for half an hour.

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[1] Diesel Engine Users' Association, May 26th, 1918.

[2] "Tars and Tar Oils as Fuel for Diesel Engines," C. Day. A paper read before the Diesel Engine Users' Association, January 19th, 1916.

[3] *Ibid.*

3. Batho's specification :—[1]

Specific gravity, between 1·0 and 1·10.
Viscosity, generally 2° Engler.
Flash-point, 100° F. to 130° F.
Colour, one drop on white paper should show no black residue, as is the case with tar.
Calorific value, between 15,800 and 16,500 B.Th.U. per 1 lb.
Ash, should not exceed 1 per cent. (unburnt residue of tar oil is mostly harmless).
Water, should not exceed 1 per cent.
Sulphur, 0·5 to 1 per cent.

The attention of the reader must be called to the fact that ammonium chloride is liable to be present in the water contained in creosote oil, and an oil containing this substance is unsuitable as a fuel for oil engines ; dissociated ammonium chloride, especially in the presence of water, is a very active corrosive agent.

As a fuel for boiler and other kinds of furnaces pitch-creosote mixtures are at times employed. There are three grades of pitch-creosote mixtures on the market, one contains 25 per cent. of pitch, another 50 per cent., and another 75 per cent. As this type of fuel is atomised into the furnace, care must be taken when manufacturing to use clean, " non-salty " creosote oil and a pitch free from dirt, sand, etc.

Creosote oils intended for the manufacture of sheep dips and disinfectant fluids must be specially prepared if the best results are desired. One of the chief points to bear in mind is the removal of naphthalene " salts." The presence of this substance has a very deleterious effect on the emulsifying power of the finished dip or disinfectant. It is one of the causes of " falling heavy," *i.e.* on addition to water, falling through the water to the bottom of the vessel instead of spreading in the form of white clouds. Naphthalene " salts " should be separated very carefully by allowing the creosote to stand a considerable time during the cold weather or, better still, by refrigeration. Some of the creosote oils obtained from the naphthalene plant prove useful in this respect.

All creosotes intended for the purpose now under consideration must contain a certain percentage of tar acids, this varying according to the requirements of the buyer. Some buyers require 3 per cent., others 5, 10, 15, 20 per cent. or more. It should be mentioned that redistilled creosote is the most suitable for sheep dip and disinfectant manufacture. Another matter for consideration is the specific gravity of the creosote. The best results are obtained, as a general rule, if the oils are of a specific gravity approaching that of water. This means that the lighter the specific gravity of the creosote the better the emulsifying power of the fluid, other things being equal. Naturally, it is not always possible to obtain a coal-tar creosote of a specific gravity of 1·000 and in any case never in large quantities, but it is possible to make a blend of a creosote, say, of specific gravity 1·055 or even of a higher or lower gravity with a fairly high distilling petroleum, say, of a specific gravity between 0·800 and 0·820. The specific gravity of the finished disinfectant fluid or sheep dip will, of course, be greater than that of water, but it must be remembered that the soap used in the preparation "dissolves" in the water, to which the fluid is added prior to being used, while the oils do not. The function of the soap in the fluid is to form a colloidal solution with water which will emulsify the oily portion of the disinfectant and keep it suspended in a very finely divided state. Other things being equal the finer the state of the emulsion the more efficient is the action of the disinfectant fluid.

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[1] The Diesel Engine Users' Association, February 23rd, 1916.

In the manufacture of the cheaper fluids rosin soap is used alone, but in the higher quality disinfectants a mixture of rosin soap with a vegetable oil soap, or a vegetable oil soap alone, is employed. The chief vegetable oils employed are castor oil and linseed oil, or their fatty acids. It must be remembered that excess of caustic alkali (caustic soda or potash) is to be avoided; it spoils the "falling" and emulsifying properties of the fluid and reduces the activity of the disinfectant by combining with the tar acids or phenols. In making a fluid the wisest plan is to let the works chemist calculate approximately the amount of caustic lye required for each pan charge and to employ a man to manufacture the fluid who possesses some knowledge of soap making.

There are numerous formulæ used for the manufacture of disinfectant fluids, each manufacturer using those which best fit in with his ideas or those of his customers. As a guide to the student, however, the following particulars may be useful.

Disinfectant fluid.	Per cent.
Rosin	26
Light creosote, sp. gr. 1·025, approx. 18 per cent. tar acids	61
Petroleum, sp. gr. 0·815	3
Caustic soda	2·5
Water	7·5

With reference to the various high coefficient disinfectant fluids now on the market, these are generally made in works other than tar distilleries, and contain as their chief ingredients blast-furnace oil tar acids specially distilled and blast-furnace creosote.

Sometimes creosote is used in the manufacture of cheap lubricating greases for colliery trucks and bogies. The oil for this purpose must be of the heavy type, and the one most frequently used is that known as strained oil or "dead" oil. This oil has been referred to already in Chapter XVIII, page 325, and is obtained during the manufacture of crude anthracene. The specific gravity varies somewhat; an oil testing 1·060 at 60° F. is frequently used. These greases are prepared by adding rosin oil and slaked lime to the green oil. Usually the composition varies between 86 to 88 per cent. of heavy oil, 4 to 7 per cent. of rosin oil, and $4\frac{1}{2}$ to $6\frac{1}{2}$ per cent. of slaked lime, the remainder being water. In the brick industry creosote sometimes finds application under the name of brick oil. For this purpose it should possess a specific gravity between 1·060 and 1·070 and be quite free from "salts."

A suitable creosote for the manufacture of black varnish (usually a mixture of coal-tar pitch, creosote and heavy naphtha, or of coal-tar pitch, water-gas pitch, creosote and heavy naphtha) must be free from an excess of naphthalene or anthracene salts, contain not more than 2 per cent. of water determined by distillation, and of a specific gravity between 1·050 and 1·065. A usual plan is to employ the higher gravity oils for slow-drying black varnishes in which more flexibility in the film of dried varnish is desired, using perhaps a good proportion of water-gas pitch in the composition. In the author's experience, however, it has been found that all films made of the pitches and bitumens (whether heavy creosote or light creosote has been used) become very brittle in a short space of time, particularly those films made from a varnish in which water-gas pitch has been used. This result is due not only to the original somewhat brittle nature of the pitch or bitumen, but also to the action of the chemical rays of sunlight and diffused light, which seems to bring about changes in the nature of the material, probably by auto-oxidation.

TABLE 66

	Specific Gravity.	Water.	Phenols.	Naphthalene.	To be liquid at	Distillation.	Apparatus.
a	1·050–1·060 at 15·5° C.	3 per cent.	10 per cent.	30 per cent. at 15·5° C.	38° C.	Residue above 315° C. 25 per cent.	Retort
b	1·040 at 27° C.	2 per cent.	8 per cent.	Not stated	32° C.	Below 315° C. Not more than 75 per cent.	Wurtz flask
c	1·040–1·050 at 15·5° C.	3 per cent.	4–12 per cent.	Not less than 20 per cent. at15·5°C.	Not stated	Not stated	—
d	1·090 at 20° C.	2 per cent.	Not stated	Not stated	25° C.	Below 315° C. Not more than 60 per cent.	Not stated
e	1·030 at 15·5 C.	3 per cent.	Do.	Do.	32° C.	Above 260° C. 25 per cent.	Do.
f	Not stated	3 per cent.	Do.	Do.	15·5° C.	No distillate below 200° C. Not more than 70 per cent. at 280° C.	Do.
g	1·000–1·030 at 15·5° C.	2 per cent.	18 per cent. min.	Nil	0° C.	Not less than 50 per cent. at 265° C. Not less than 80 per cent. at 315° C.	Do.

As a wood preservative creosote oil is, without doubt, the finest material extant, and more of it is used for the preservation of railway sleepers and other timber in connection with railway work, and also timber used in telegraph installations, than in any other direction. It may be added here that the United States of America are the largest consumers of this material, using upwards of 108,000,000 gallons per annum. Large quantities are, of course, supplied to the British and Continental railway companies by manufacturers in this country, in addition to exporting very considerable quantities to the States. All this creosote is sold according to specification, each buyer having his own. This will, of course, necessitate in many cases careful mixing of several grades of oil, and even the removal of a certain amount of tar acids and sometimes the whole of the naphthalene. In other cases it is often necessary to add naphthalene before the creosote will answer the requirements of a certain specification. In order to give some idea of the various requirements of specifications, several are given in Table 66, and three other specifications for creosote, such as used on some American railroads, are given in 67. See also Chapter XXII, pages 397–411.

TABLE 67

Grade.	Sp. gr. at 38° C.	Liquid at	At 200° C.	Distillation.			Water.
				210° C.	235° C.	355° C.	
No. 1	At least 1·03	38° C.	None below	Not over 5% below	Not over 25% below	Above, if exceeding 5% must be soft	Not over 3%
No. 2	Do.	38° C.	Do.	Not over 8% below	Not over 35% below	Do.	3%
No. 3	Do.	38° C.	Do.	Not over 10% below	Not over 40% below	Do.	3%

It is not convenient to discuss here whether a creosote containing a high percentage of naphthalene and tar acids or one containing a small quantity of tar acids and no naphthalene will give the best results as a wood preservative. According to many investigators excellent results have been obtained with both kinds, and at present the matter will have to be left at that so far as this book is concerned. Tests to prove the efficiency of a creosote for railway work take a number of years, and weather and soil conditions, etc., will influence the results in a variety of ways.

H. Schmitz and S. M. Zeller[1] investigated different fractions of coal tar creosote in order to find the one which possessed the most toxic action upon fungoid growths, and they considered that a fraction boiling between 270° and 315° C. was the most effective. According to their experiments, any material distilling above 355° C. is practically valueless.

In the important process of stripping gas of its benzole, creosote has found a use, and it is probable that as time goes on the quantity required for this purpose will increase. The quality of the creosote destined for this purpose must receive careful consideration, especially in connection with the content of water and salts. Not more than traces of water should be allowed, and if the best results are desired there should be an entire freedom from naphthalene or anthracene salts. In regard to the specific gravity, this varies according to conditions laid down by different users, the variations being between 1·01 and 1·050. The distilling range varies for a similar reason. Some users prefer a creosote of a specific gravity between 1·01 and 1·02, which, when submitted to a distillation in a retort yields 85 to 90 per cent. under 300° C. Others one of a specific gravity of about 1·035, and which will not begin to distil below 200° C. and yields 70 per cent. between this point and 280° C., when distilled in a retort. P. D. Walmsley and H. A. Morfey[1] give the following as a representative test of a suitable creosote for benzole recovery purposes.

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[1] *Jour. Ind. Eng. Chem.*, 1921, 13, 621–623.

Distillation portion of test carried out in a retort with the bulb of the thermometer immersed in the creosote.

Specific gravity	1·035
Dropping point	210° to 220° C.
50 per cent. distils over at	250° C.
80 ,, ,, ,,	300° C.
Water content	traces.

On cooling the distillate obtained up to 300° C. to 45° F., and maintaining this temperature for thirty minutes, the solid naphthalene settling out, on being filtered and pressed, should not amount to more than 7 per cent.

Dr. Colman's specification of a creosote oil suitable for the oil washing of gas is as follows :—

Specific gravity at 60° F.	1·010 to 1·030.
Tar acids	Immaterial.
Naphthalene	Should deposit no naphthalene on being cooled down to 55° F.
Boiling-point	Should not boil below 200° C.
Distillation	Should distil not less than 70 per cent. up to 300° C. nor more than 90 per cent.

For storage of creosote second-hand boilers may be used. Very frequently large tanks built of iron plates or reinforced concrete, as described in Chapter V, are provided for this purpose, and it is policy to cover them. A closed steam coil, or coils, must be placed in the tanks, the diameter of the tubing varying between 1 inch and 2 inches according to the size of the storage tank. At convenient points in the suction and delivery mains to and from the storage tanks a 1-inch steam inlet should be fitted. This will enable the pump man to clear the mains with open steam after pumping, a most necessary procedure when "salty" creosote has been passed through the mains.

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[1] "Some notes on Benzol Recovery and Rectification." Read before Manchester District Institution of Gas Engineers, October 28th, 1916. *Gas World*, November, p. 410.

The fact that creosote is volatile and that this volatility does not depend upon the presence of naphthalene altogether, if at all, must be borne in mind when considering the question of storage. A few rough volatility tests carried out by the author will illustrate this point (see Table 68). Flat dishes 6 cm. in diameter were employed, giving a surface area of approximately 28·25 sq. cm., and the material was placed in the dishes to a depth of 0·5 cm. Some creosote oil was freed from tar

TABLE 68

Hours' exposure.	Creosote free from tar acids and naphthalene.		Creosote containing 10 per cent. tar acids and 25 per cent. naphthalene.		Ground candle naphthalene.	
	Loss at 60-65° F.	Loss at 100° F.	Loss at 60-65° F.	Loss at 100° F.	Loss at 60-65° F.	Loss at 100° F.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
24	1·38	3·42	1·10	3·30	—	1·00
48	2·42	6·10	—	—	0·90	2·20
96	4·61	10·40	4·10	11·60	2·31	3·32

TABLE 69

°Tw.	Sp. Gr.	Gals. per ton.
25	1·125	199·11
24	1·120	200·00
23	1·115	200·89
22	1·110	201·80
21	1·105	202·71
20	1·100	203·63
19	1·095	204·56
18	1·090	205·50
17	1·085	206·45
16	1·080	207·40
15	1·075	208·37
14	1·070	209·34
13	1·065	210·32
12	1·060	211·32
11	1·055	212·32
10	1·050	213·33
9	1·045	214·35
8	1·040	215·38
7	1·035	216·42
6	1·030	217·46
5	1·025	218·53
4	1·020	219·60

acids by extraction with caustic soda, and naphthalene by chilling to 0° C. and filtration, and the specific gravity of this treated oil was 1·035. A portion of this oil was used in the test in this state while to another portion was added tar acids and naphthalene, as indicated in Table 68, before submitting to the same conditions of test.

With reference to the methods of testing creosote oil, unfortunately at the present day there are no standards, and to a large extent each chemist uses his own method for the determination of one or more constants. Some of the tests in use are given in Chapter XXII.

Table 69 which gives the degrees Twaddell, specific gravity and gallons per ton will, no doubt, be found useful for reference when dealing with creosote.

The following particulars may be useful to students and others.

Co-efficient of cubical expansion of heavy creosote.

Oil liquid at 0° C. *Specific Gravity* 1·0654.

Determinations made in a 100 c.c. Regnault specific gravity bottle with narrow neck. Calculations made by the use of the following expression :—

$$\frac{w}{(W-w)}\,t^\circ$$

in which W=original weight. w=loss of weight.
t°=number of degrees through which creosote was heated.

	Co-efficient of cubical expansion.
Between 0° and 20° C.	0·000678
,, 20° and 40° C.	0·000677
,, 40° and 60° C.	0·000765
,, 60° and 80° C.	0·000691
,, 80° and 100° C.	0·000775
	mean=0·000717 per °C.

or 0·000398 per °F.

CHAPTER XXI

GAS STRIPPING

Shortly after the commencement of the great European War in 1914, there became an increased demand for toluene which was required for the manufacture of explosives, and many gas companies adopted a system of washing their gas with tar. This system, known as the " C " process, removed some of the benzene and toluene from the gas and, of course, increasing the percentage of these materials in the coal tar. The following figures will illustrate this : Normal tar from vertical retorts (intermittent system) yielded 0·75 gallon of toluole per ton, whilst a tar from the same system after being employed in the " C " process yielded 2·49 gallons of toluene per ton. Several workers have found that the addition of a small quantity of powdered limestone to the coal before carbonisation increases the yield of toluene in the tar, especially when used in connection with the " C " process. G. Stevenson[1] of the Long Eaton gasworks gives the following figures, Table 70, which illustrate this statement. In each case the coals used were low-grade Tupton " Derbyshire " seam, the temperatures used in carbonisation were the same, and the results were not obtained at the expense of either the quality or quantity of the gas. In each determination 9,000 c.c. of tar were taken.

TABLE 70

	Normal Carbonisation "C" Washing.	Limestone used No "C" Washing.	Limestone used plus "C" Washing.
Crude naphthas . . .	176 c.c.	320 c.c.	508 c.c.
Middle oils	720 c.c.	850 c.c.	800 c.c.
Toluene in tar, lbs. per ton of coal	0·27	0·41	1·01

In the " C " process the temperature of both the gas and the tar have an important bearing on the amount of benzene hydrocarbons taken up by the latter ; the higher the temperature the less the amount given up by the gas to the tar. The temperature of the gas at the gas inlet to the washer should be about 65° F. and that of the tar inlet about 60° F. This will mean that the tar must be cooled as well as the gas, and unless the cooled tar is thin like vertical retort tar, more or less unsuccessful working will result. The tar can be cooled by passing through a series of pipes which are water cooled by allowing cold water to trickle over them. Washers similar to those used for the removal of ammonia from gas are quite suitable for the carrying on of the " C " process.

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[1] *Gas World*, January 29th, 1916, p. 103.

The amount of tar made at the gasworks is not sufficient to remove the whole of the benzene hydrocarbons from the make of gas, and according to Geoffrey Weyman[1] the maximum efficiency of the " C " process is about 50 per cent., at which about 0·15 gallon of toluene and 0·9 gallon of benzene are left in the gas.

A far older and much more efficient and satisfactory process is that of gas stripping by the use of a suitable wash oil. It appears that Caro in 1869 was the first worker to use tar oils to remove benzenoid hydrocarbons from coal gas. Later, in 1882, George E. Davis and Josiah Hardman each patented a process for recovering benzole from gas by the use of tar oils, the former working his process in Manchester and the latter at Thorncliffe. Shortly after this coke oven works owners began to consider the recovery of the by-products from their coke ovens, and much experimental work was done in connection with the recovery of benzole from the gas, based on the ideas of the pioneer workers just mentioned. This experimental work has resulted in the production of some very efficient processes.

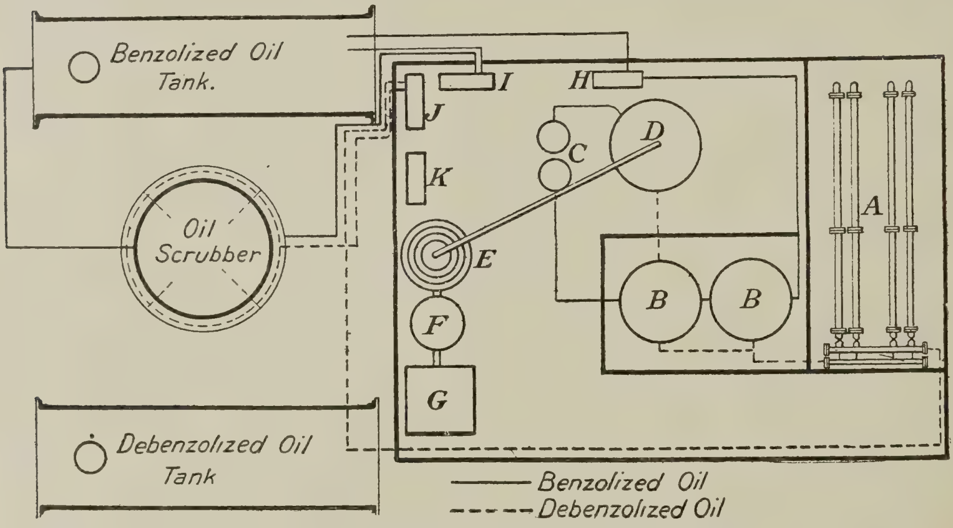

Fig. 118.—Diagrammatic Plan of General Arrangement of Gas Stripping and Crude Benzole Recovery Plant.

Owing to the late European War, the process of gas stripping was introduced into gasworks practice, and many gasworks are still carrying it out at the present day. It is highly probable, if the adoption becomes general, that a yearly production of about fifty-five million gallons will result. At the outset there were fears that the stripped gas would displease the consumer and would prove unsuitable for use in the flat-flame burner, but these fears have not been realised. Partly debenzolised gas has proved quite suitable as a heating medium and for lighting purposes, the gross B.Th.U. being reduced only about 4½ per cent., and with a modified flat-flame burner it gives quite satisfactory results. Needless to say, with a gas mantle, the result is all that can be desired. Completely stripped gas can be enriched by the use of carburetted water gas, or by spraying it with paraffinoid hydrocarbons.

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[1] " The Effect of the War on Gasworks Practice." Before North of England Gas Managers' Association. *Gas World*, May 13th, 1916, p. 444.

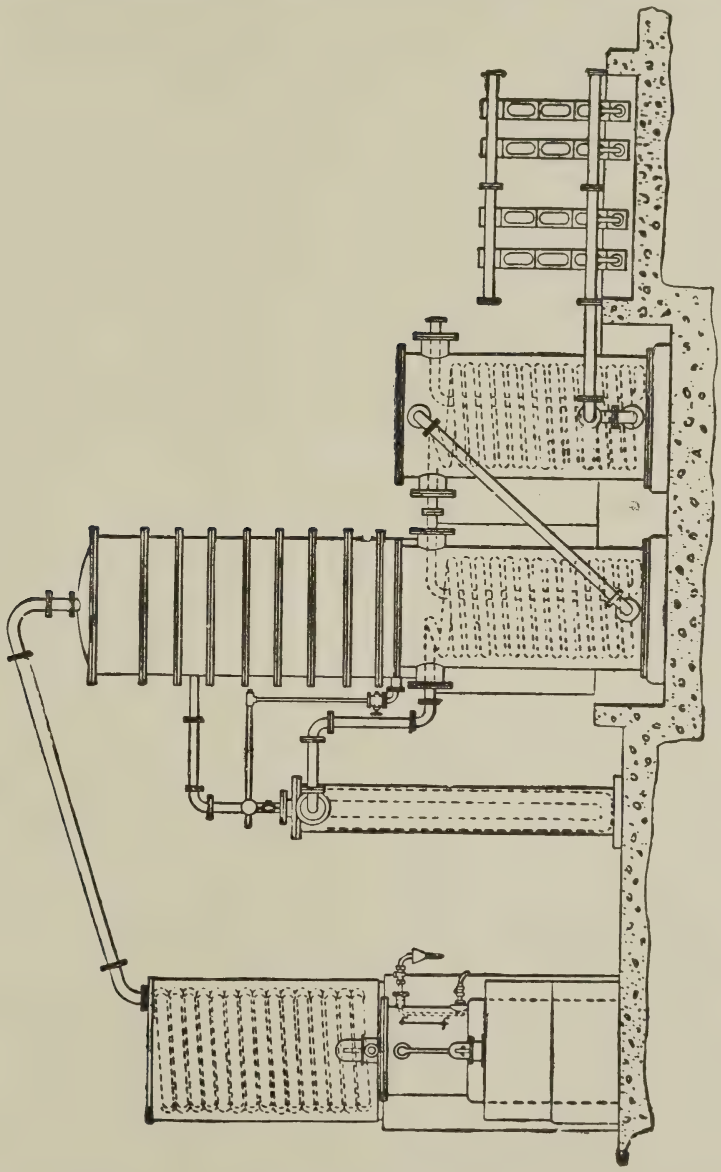

Fig. 119.—Elevation of Crude Benzole and Toluole Plant (Portion of Gas Stripping Plant).

The plant required for stripping coal gas and debenzolising the wash oil need not be a complicated one. Briefly, it consists of a washer or scrubber, a benzolised oil tank, heat exchangers, preheaters, still, condenser, separator, receivers for crude benzole, oil coolers, a debenzolised oil tank and the necessary pumps. Reference to Figs. 118, 119 and 120 will give the reader an idea of the arrangement of this plant.

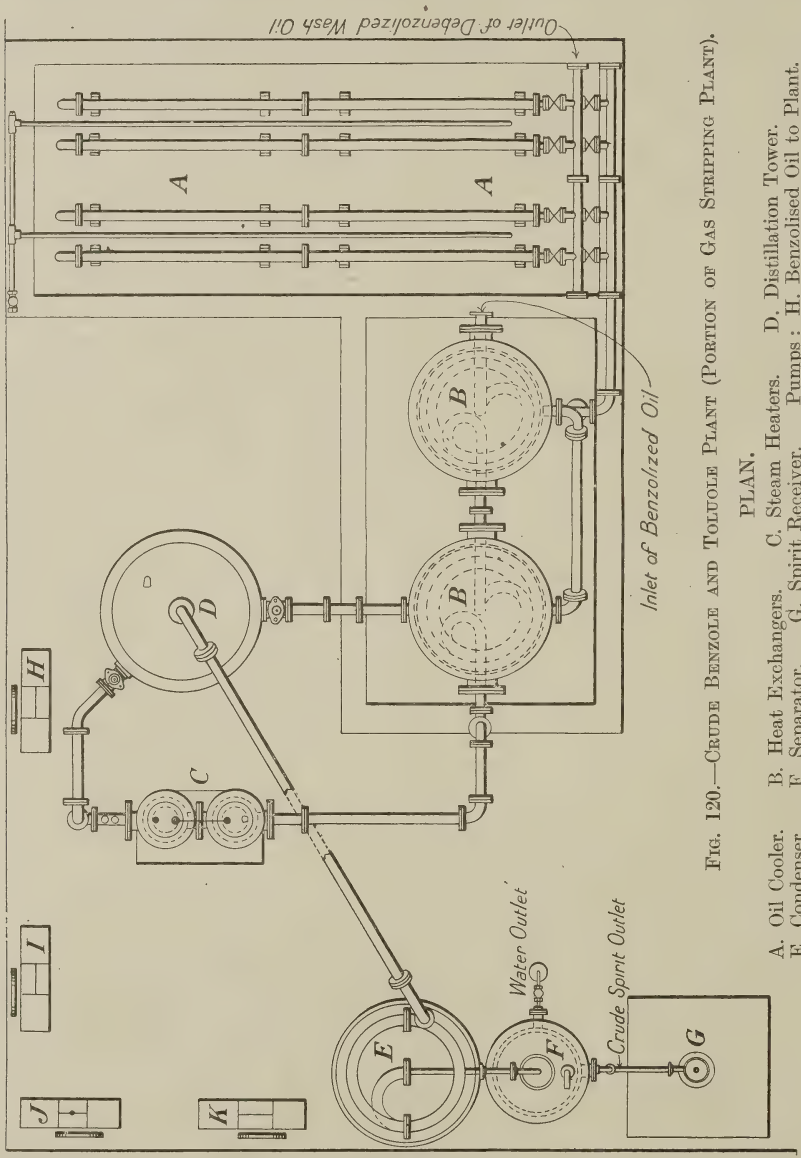

FIG. 120.—CRUDE BENZOLE AND TOLUOLE PLANT (PORTION OF GAS STRIPPING PLANT).

PLAN.

A. Oil Cooler. B. Heat Exchangers. C. Steam Heaters. D. Distillation Tower. E. Condenser. F. Separator. G. Spirit Receiver. Pumps: H. Benzolised Oil to Plant. I. Benzolised Oil to Scrubber (Re-circulation). J. Debenzolised Oil to Scrubber. K. Spirit to Storage.

With reference to the kind of washer or scrubber, this may be of any efficient type as now employed in a gasworks for the purpose of ammonia recovery. The ordinary tower scrubber filled with boards, the Livesey washer, the Walker purifying apparatus with rocking arrangement, and several types of rotary scrubber have been used with success. In the case of the scrubber filled with boards it is as well to distribute the wash oil at the top of the apparatus by means of several Gurney's jets. Provision must be made, say, by the use of T-pieces and plugs, to allow the jets to be poked through with a wire should they become obstructed, and it is also necessary to supply the wash oil at a pressure sufficient to cause a forcible impinging on the discs of the jets. If this is not done the oil will not be sprayed in an efficient manner. Some works made an arrangement so that the upper half of the washer be supplied with debenzolised oil and the lower half with recirculated partly debenzolised oil. In the author's opinion this is not an efficient method and is quite wrong in principle. In other works two separate washers are employed, one for the debenzolised oil and the other for partly benzolised oil, providing for the unwashed gas to enter first that washer supplied with the partly benzolised oil. As the efficiency of the stripping process depends, in addition to the adoption of a strict counter-current system, upon the reaction surface presented by the packing in the scrubber and the length of time the gas and wash oil are in contact, due consideration must be given to these matters and a scrubber put in of sufficient size to deal with the daily make of gas in a satisfactory manner. Dealing with a scrubber packed with the

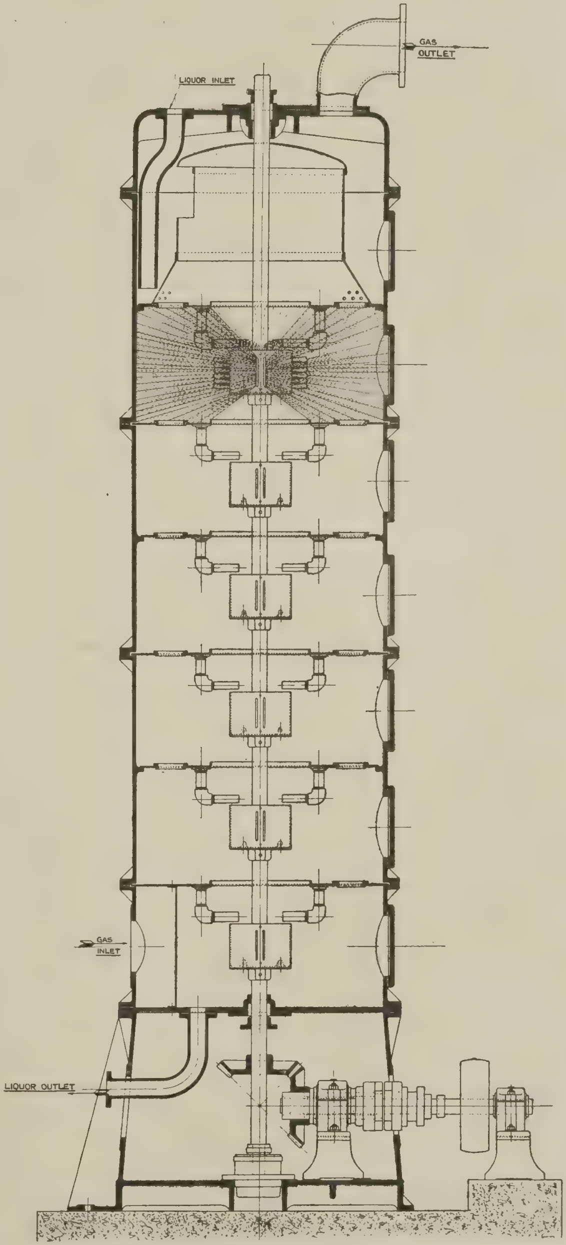

Fig. 121.—Blair's Centrifugal Scrubber.

usual wooden boards, a surface area (reaction surface) of between 500 and 550 square feet should be allowed for each ton of coal carbonised per diem. These figures correspond approximately to 16 cubic feet and 18 cubic feet of tower space respectively. In order to properly control the supply and keep a constant head of wash oil, a feed tank of suitable size should be erected above the scrubber.

In Fig. 121 is illustrated "Blair's" centrifugal scrubber, a piece of plant of entirely new principle. For the recovery of benzole from coal gas it is an exceedingly efficient type; the average efficiency when extracting benzole at 4 per cent. concentration in coal gas is approximately 90–95 per cent. The following figures relate to a plant supplied to a coke oven recovery works :—

Gas treated per hour.	Benzole in gas per cent.		Percentage of efficiency.
	Before.	After.	
Cub. ft.			
90,000	4·0	0·2	95
125,000	3·7	0·35	90
150,000	3·5	0·3	91

The diagram is self-explanatory in so far as the mechanical portions are concerned. The method of action is as follows :—The washing medium is led in at the top of the scrubber and is carried by means of the top bevel division plate to feed pipes fitted thereon, and through these into the top distributing device. From this device it is driven by centrifugal force, emerging in the form of a very fine mist. As pointed out in another part of this chapter, see page 366, to secure the greatest efficiency the reaction surface between the wash oil and the gas must be as large as possible and the time of contact as great as can be allowed in economical works practice.

To reduce the wash oil to a fine mist is the most correct method. When a liquid is broken up, in air, into small particles these assume the spherical shape, and as the sphere is the body which exposes the minimum surface for a given volume it is necessary to break up the liquid into spheres of the smallest size possible. This is done by converting it into a mist.

The other point is the increased time of contact during the passage of the gas through the scrubber, and this is secured by the swirling motion imparted to the gas and wash oil mist; the effect of centrifugal force produced by the rapid rotation of the devices.

For efficient washing gas slip must be reduced to a minimum, and in the type of scrubber now being described this is reduced to a practical impossibility, as the whole of each chamber is filled with wash oil mist. Another important point is the fact that the whole of the chamber space is in effective commission, the amount of wash oil on the division plates being very small; in fact, just that quantity which is continuously running from the bottom of each chamber in order to keep the respective devices charged and maintain a constant flow of wash oil through the scrubber. As will be seen from the diagram the actions just described take place in all the chambers of the scrubber.

The consumption of power for each scrubber is very small, as the moving parts are all well balanced and work in ball bearings, also the back pressure thrown is very low owing to the swirling action given to the gas by the revolving liquor-atomising devices. In support of these statements the following example is given—three 10,000,000 cubic feet per day scrubbers of this type took under 5 b.h.p. to drive and threw less than 4 inches of water pressure.

Oil scrubbers and benzolising columns can be packed with Lessing or Raschig rings. In connection with the former, some tests were made during the European War for the Explosives Department of the Ministry of Munitions, with the object of comparing the efficiency of ring-filled columns with the ordinary type of column of double the size. It was found that the benzolising efficiency was raised from 66 per cent. to 90 per cent., with the yield of a crude benzole of which 80 per cent. boiled below 120° C., as against 70 per cent. with the old still of double the size.

The benzolised and debenzolised oil tanks may be of any suitable shape and size Cylindrical tanks made from second-hand steam boilers from which the tubes have been drawn and the ends blanked will serve this purpose admirably. A manhole must be provided for the purpose of cleaning, etc., and also a hole for the inlet pipe at the top of the tank and another for the outlet pipe with its centre about 4 inches from the bottom.

Most benzole recovery plants have heat exchangers and steam heaters, through which the benzolised oil passes before it enters the still; others are provided with a preheater only, and there are cases in which these pieces of apparatus are dispensed with and the benzolised oil flows direct into a fire-heated still.

Heat exchangers are for the purpose of assisting in the cooling of the debenzolised oil after it leaves the still, and the heating of the benzolised oil in its progress towards that piece of apparatus. They consist of covered cylindrical or other suitably shaped tanks of cast or wrought iron or mild steel, into which are placed coils of pipe constructed of either cast or wrought iron. Wrought-iron tanks and coils are suitable only in cases in which corrosion is slight, but when it is to be feared that ammonium salts, such as the chloride, are likely to be carried through the plant, then it is wise to use cast iron, as this metal resists the corrosive action of ammonium chloride and other ammonium salts better than does wrought iron. In order to facilitate the cleaning out of the tank, say, after brushing down the coil, there should be provided a 1½-inch or 2-inch cock at the bottom; the slurry can then be flushed out through the cock. The hot debenzolised oil passes through the tanks and the benzolised oil through the coils, the former losing heat and the latter gaining it during this progress. The inlet for the debenzolised oil is placed at the top of the side of the tank and the outlet near the bottom. The coil inlet and outlet are at the top of the tank, and the coil is so arranged that after it enters the tank it falls in a straight piece to the bottom and then rises in the form of laps until it reaches the outlet. It is unwise to make the laps too close together; a distance of about 3½ inches between each lap must be allowed, and the outside of the coil should not be less than 6 inches from the inside of the tank. Some heat exchangers are of the tubular type, *i.e.* a series of straight tubes held in position by two end or tube plates, the whole being surrounded by a cylinder provided with two covers.

In some plants the hot debenzolised oil circulates through the coils of the heat exchangers and the benzolised oil which is to be heated through the tanks, and in cases like this it is recommended[1] to fit a vapour pipe to the cover of the tank to conduct away any benzole vapours which may be formed to a condensing coil, and also to put in a baffle chamber to prevent any wash oil being carried over into the condensing coil.

The object of the preheater is to raise the benzolised oil to a temperature just before entering the still at which the maximum amount of crude benzole will be removed from the oil, and which will prevent the entanglement of water by the wash oil and enable the oil to leave the still carrying a minimum quantity of water. A preheater consists of a covered cylindrical, square or rectangular tank, containing a steam coil arranged in the form of laps. In cases in which corrosion is anticipated the tank and coil must be of cast iron for the reason just mentioned when dealing with heat exchangers, otherwise the tank may be of mild steel and the coil of wrought-iron steam pipe. Where corrosion has to be considered J. A. Wilson[2] recommends the following as a good construction for a preheater. A rectangular tank " built up of a few strongly flanged sections, with cast-iron U-pipes for the steam, these to be free at one end and jointed to the outside of the still at the other, the pipes being connected to each other by short U-bends, and being fixed horizontally, so that the oil will have an impinging action on them in its upward flow through the preheater." This worker advises against the use of gilled steam pipes, as they readily collect solid matter as it is deposited from the oil and thus reduce the heating efficiency of the coil. As a deposit of some sort is likely to form on any type of steam pipe it is advisable to arrange for a means (an easily removed cover, for instance) by which the coil can be brushed down from time to time, and in this connection it is a good plan to fit a 1½-inch or 2-inch cock to the bottom of the tank, through which the slurry can be removed. The laps of the coil should not be too close together ; a distance of at least 4 inches being allowed between each lap. The inlet for the benzolised oil is on the side near the bottom of the preheater tank and the outlet on the opposite side near the top. It is advisable to fit a vapour pipe to the cover in order that any crude benzole vapours which come off from the heated benzolised oil may be conducted to a condenser coil. It can be so arranged that this vapour pipe leads to the condenser coil which is connected to the vapour pipe of the still.

Where it is intended to adopt fire heating for the purpose of distillation a still of the pot type can be used, similar in construction to that illustrated on page 132, Fig. 30, but without the internal steam pipes. It is constructed of wrought iron or mild steel plates, with a cast-iron swan neck and vapour pipe. In setting the still there is no need to put in a curtain arch.

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[1] *Gas World*, November 18th, 1916, p. 460.

[2] " Some points in the Recovery of Benzole." J. A. Wilson, read before the Coke Oven Managers' Association, Midland Section. See *Gas World*, Coking Section, December 2nd, 1916, pp. 11–14.

The best kind of still, and the one used in the larger number of plants, is of the continuous type, and it consists principally of a tower built up of cast-iron segments or chambers. The design of these segments varies a little according to the ideas of the makers, but broadly speaking there is a great similarity. Each segment, with the exception of the top and bottom ones, has a plate cast on it, and each plate is provided with one or two overflow pipes, and several inlets over which are placed hoods or dispersers. The inlets and overflow pipes are so arranged that a seal of oil remains on each plate. As a matter of fact, the illustration of the column on page 253 gives a typical idea of the arrangement. The segments, with the exception of the top and bottom ones, are approximately 1 foot deep and 3 feet 9 inches to 4 feet in diameter, flanged, and provided with perfectly faced joints. The top segment is simply a shallow dome with an outlet cast on the top, in the centre, to which is fixed the vapour pipe. With regard to the bottom segment, this is much larger than those which compose the greater part of the still, and there is no plate cast on it. Approximately the size is 3 feet 9 inches deep. On this segment are cast an outlet for the debenzolised oil and an inlet for the live steam supply. In some cases there is a second inlet for the purpose of introducing a steam supply to a closed steam coil. This latter arrangement is considered by many workers, and also by the writer, to be an advantage. The live steam is introduced into the still by means of two jets or a small, open steam coil provided with a few perforations. On the third segment from the top is cast an inlet to which is connected the benzolised oil supply. It should be mentioned here that some stills are provided with a baffle chamber (which is fitted to the top segment) and on the top of which is fixed a vapour pipe. In cases like this the inlet for the benzolised oil is cast on the top segment of the still proper. The number of segments provided with plates varies somewhat according to the make of the still, but a good average is twelve when the still is not provided with an " outside " dephlegmator. If it is desired to connect a dephlegmator to the still, then the latter must not be too high, *i.e.* there must not be too many segments in its construction, or else dephlegmation will take place where it is not wanted, that is in the still. The number of segments in cases like this should be about eight.

The purpose of an " outside " dephlegmator attached to the still is to remove much of the naphthalene from the wash oil and also to prevent it getting into the crude benzole. This excellent idea was advocated strongly by the late Mr. G. Stanley Cooper, a clever and much respected worker, especially in matters relating to the coke oven and by-products industry. The construction of the dephlegmator varies according to the ideas of the maker or the designer. One type is very similar to that illustrated and described on pages 260 and 261. The diameter is, however, rather greater, being about 3 feet, and the overall length less, varying between 4 and 5 feet, and the water tubes are not quite so close together. Another type of dephlegmator is built up of several cast-iron segments, each water jacketed and provided with a plate on which are inlets, hoods, and overflow pipes. The number of segments containing plates varies, but it is usually between five and six. In the tube dephlegmator the vapours from the still enter at the side, near the top, and the uncondensed vapours leave at the side, near the bottom, but in the plate type the vapours enter the side of the bottom segment and the uncondensed portion leaves at the top from an outlet cast in the centre of a shallow dome which is bolted on to the top section. In both types the condensed liquid, oil containing a quantity of naphthalene, leaves at the bottom and is conducted away to cooling tanks in which the naphthalene separates out. It is not wise to place the dephlegmator too far away from the still ; a distance of about 4 feet is quite enough.

Cooling tanks for the purpose of receiving and cooling the oil which leaves the dephlegmator, in order that its excess of naphthalene may separate out, should be constructed of mild steel plates and erected under cover, but away from any source of heat. They should be shallow, say, about 2 feet deep, and of any suitable length and width to suit the volume of oil to be dealt with. If a means of refrigeration is already in existence and an extension can be conveniently made to these tanks, it will be an advantage, so far as speed and complete separation of naphthalene are concerned, to use it. Circulating cold water through pipes resting on the bottom of the tanks acts fairly well in the summer time.

The condenser attached to the still consists of a length of wrought-iron tubing or several lengths of cast-iron pipe arranged in the form of a number of laps and placed in a cylindrical, square, or rectangular tank according to convenience. Condenser tanks and coils have already been dealt with on pages 150–152 and 262.

A description of a suitable separator or divider will be found on page 154.

As a receiver for the crude benzole a cylindrical, square, or rectangular tank constructed of mild steel plates can be used, according to convenience. It must be a covered tank, the joints of which should be double riveted and well caulked. On the top of the tank is a manhole with a tight-fitting lid, a hole, say, 1½ inches, for the inlet pipe and a ½-inch hole which acts as an air vent and which can also be used for dipping purposes. This hole must be closed with a plug when not in use. A 2-inch outlet pipe is fitted on the side of the tank with its centre about 3 inches from the bottom, and it is as well to fit a 1½-inch drain cock on the bottom of the receiver. This will be found useful for cleaning purposes.

Oil coolers vary somewhat in construction. In some plants they consist of a number of flanged cast-iron pipes, placed horizontally, and connected with U-bends, and arranged in tiers of six or more, or on the flat in a tank. In the case of the former arrangement the bottom tier of pipes is suspended in a tank, generally constructed of concrete, and all the pipes are water cooled, the upper tiers by means of water sprays or water trickling over them and the bottom layer by the water in the tank, which must, of course, be kept on the move. In the latter arrangement the pipes are totally immersed in water, of which there must be a plentiful supply passing through the tank. With reference to the area of cooling surface, see page 368.

Sometimes the cooler is constructed in a similar manner to an ordinary still condenser and placed in an upright position, or else it consists of a number of tubes swelled into two tube plates and fitted into a cylindrical iron vessel, the whole arrangement being placed in a vertical or horizontal position.

Pumps may be of any reputable make, either of the ram or centrifugal type. So far as efficiency is concerned the latter type of pump is the better to use, and as they are designed for high lifts, from 25 to 50 feet or even more, there need be no fear on this score. A special type of rotary pump suitable for dealing with wash oil is now on the market. It is capable of pumping oil at a temperature of 120° C. and can be used with a suction lift of up to 8 feet. This pump is made by the Roots Company of Connellsville, and according to the makers 75 to 85 per cent. of the power applied to the operating shaft is absorbed in doing useful work.

It is a wise plan to provide a means by which the supply of debenzolised wash oil to the scrubber and also the supply of benzolised oil to the still can be controlled. This can be done by the use of a meter and a cock provided with a quadrant, feeding by gravity from a tank in either case. A gauze sieve must be placed before the inlet to the meter for the purpose of keeping back particles of solid matter, and the sieve should receive regular inspection to see that this material is removed from it. With reference to the meter, a certain amount of trouble may arise in regard to corrosion, but there is no doubt that with proper representation makers will be induced to construct meters of a specially resistant metal.

Blair, Campbell and McLean's benzole recovery plant is illustrated in Fig. 122. In this plant the benzolised oil leaves the feed tank A and passes through a special oil regulator provided with an automatic float valve, then through an oil meter D, and from this piece of apparatus to the tubular preheater E. Should any extraordinary back pressure take place in the plant the automatic float valve of the oil regulator comes into action and immediately cuts off the oil flow. In the preheater the oil is raised to a temperature of about 90° C., by means of the outgoing vapours from the still. From the preheater the oil flows to the tubular heat exchanger F. This piece of apparatus is connected to the debenzolised oil outlet of the still, a matter of importance, as the quantity of steam required for heating the benzolised oil before passing into the still, and also the amount of water for cooling in the case of the oil coolers, is much reduced, and consequently smaller vessels are needed in each case. On leaving the heat exchanger the oil passes into the superheater G, in which its temperature is raised to approximately 130° C. The superheater is of special design, the steam coil being arranged in halves, and each half made interchangeable. By doing this the scrapping of the full length of coil is obviated when the top or bottom portion becomes so corroded that its removal is necessitated. Corrosion is most probably brought about by the presence of small quantities of ammonia, ammonium sulphocyanide, ammonium chloride, and carbon disulphide in the wash oil, assisted by water vapour and an elevated temperature. It is thought probable that the carbon disulphide and ammonia present may form ammonium sulphocyanide according to the well-known reaction:

$$3CS_2+8NH_3=NH_4CNS+(NH_4)_2S_3+2NH_4CN+2H_2S.$$

Fitted to the superheater is a vapour pipe which conducts any benzole vapours

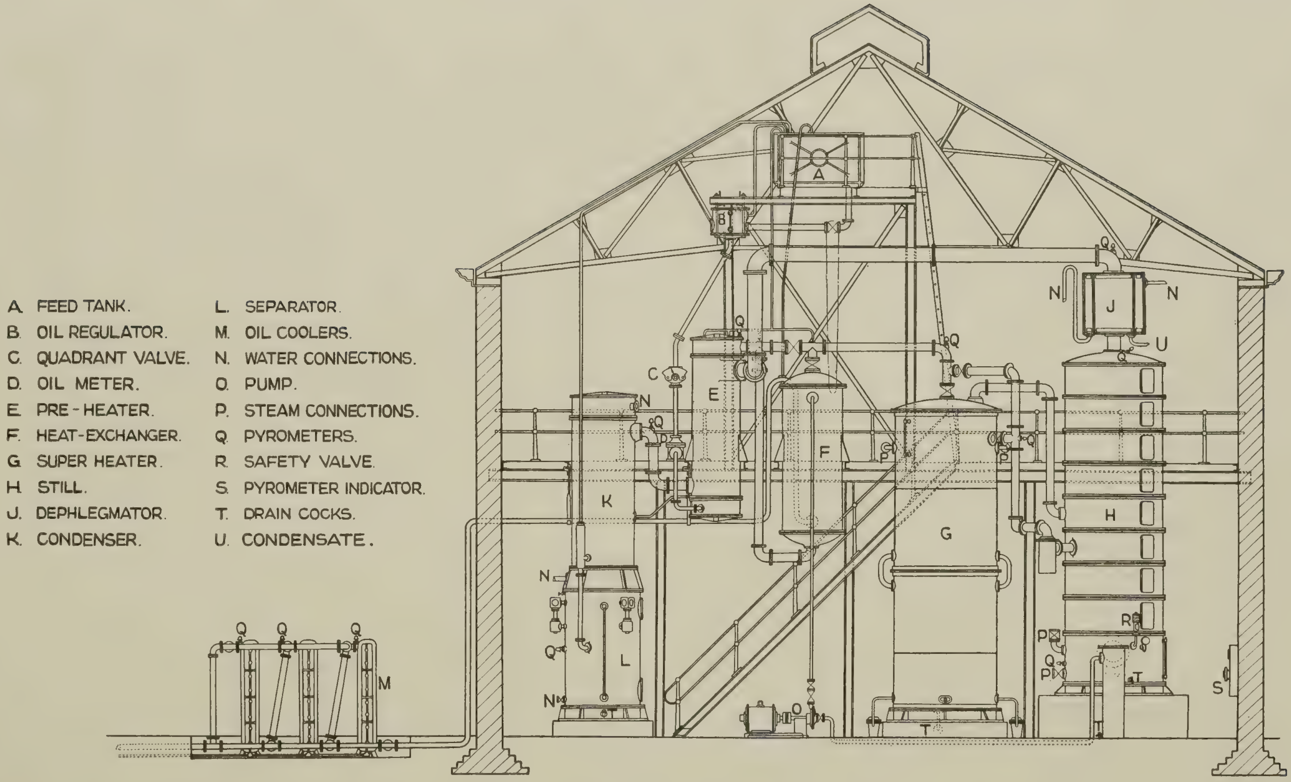

FIG. 122.—BLAIR'S BENZOLE RECOVERY PLANT.

away into the higher sections of the still. The oil, on leaving the superheater, flows into the still at about its middle section. Here and during its travel downwards through the fractionating plates it meets with steam, which enters the still at the bottom via a detachable perforated coil. On the arrival of the oil at the bottom of the still it is conducted through a seal pot to a pump O, and is pumped into the heat exchanger F, and from this piece of apparatus it is run to the oil coolers M.

The still is built up of cast-iron sections, each of which has division or fractionating plates cast in the middle of and fixed between alternately. The vapour passages in the plates are fitted with bells of an improved type which ensure a large vapour area, and consequently thorough and intimate contact between vapour and liquid. The bells are spaced at correct distances so as to ensure the maximum deformation of the bubbles, a most important consideration for efficient results.

The vapours of benzole, etc., driven from the oil by the steam, ascend through the fractionating plates and eventually arrive at, and pass into, a special dephlegmator J of the horizontal type. In this piece of apparatus the heavier oils and naphthalene (which remains in solution in the oils) are separated. The non-condensed benzole and water vapours pass out of the dephlegmator through the vapour pipe to the preheater E, and then leave this piece of apparatus and enter the tubular water condenser K. Here they are condensed and flow into an automatic separator which divides the benzole from the water, the former running to a storage tank and the latter to waste. It will be noticed from the diagram that the condenser is placed above the separator, thus economising floor space. A noxious gas separator is provided through which these gases pass before entering the atmosphere.

A great improvement in this plant is the fact that it is fitted with pyrometers connected with indicator apparatus so that all temperatures can be read at one point. Further, a thermostat can be fitted to the still, thus automatically controlling the heating.

W. H. Wright[1] states that in the United States of America the general type of scrubber used in the recovery of benzole from coke oven gas is in the form of a tower, varying from 6 to 24 feet in diameter and 40 to 90 feet high, and uniformly fitted with wood grids. In a unit of plant three such towers are placed in a series. The wash oil is circulated in counter-current to the flow of gas, and sufficient quantity is employed to produce a wash oil of 2 to 3 per cent. benzole content. Petroleum oils of high boiling-point are used for washing, and the time of contact of the oil with the gas in the large number of plants is between 70 and 100 seconds. The temperatures of the gas and the wash oil are kept below 25° C., as at about this temperature the absorbing power of the oil begins to drop off very rapidly. The benzolised oil passes first through a vapour-to-oil heat exchanger and then through an oil-to-oil heat exchanger. Wright suggests the use of ammonia refrigeration for cooling the wash oil, also that the cooling be brought about with the wash oil inside the tubes and the cooling medium outside until a temperature of about 4·5° C. is reached, and then finishing the cooling with the oil outside the tubes and the cooling medium inside.

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[1] Amer. Gas Inst., see *Gas Jour.*, 1917, 140, 462.

The plant used in working up crude benzole, and that employed in making rectified benzole and toluole, has already been described in Chapter XII, and the reader is referred to it for information on this subject.

There are several advantages secured by using oil instead of tar to recover the lower benzenoid hydrocarbons from coal gas. The chief of these are :—

1. Variation in atmospheric temperature does not seriously affect the efficiency of the process; during the winter months the oil does not thicken up like tar.
2. The stripping of the gas can be carried out to completion or partially, as desired.
3. If the process is properly worked naphthalene is removed from the gas in a very efficient manner.

The benzole recovery process is a continuous one, the wash oil first passing through the scrubbers and from these to the benzolised oil tank, thence onward through the heat exchangers and superheater to the still. In the still the benzolised oil is relieved of its crude benzole, and then it passes through the heat exchangers and from these to the air coolers and finally to the debenzolised oil tank. From this receptacle it is pumped to the first scrubber and from this piece of apparatus the whole process is repeated. The wash oil continues in circulation until it becomes "spent" oil, which is thicker and its specific gravity and distilling range higher than that of the original "fresh" oil. It is then replaced by a fresh supply, or else a certain percentage of the wash oil is removed from circulation at regular intervals, the same amount of "fresh" oil being added.

The quality of the wash oil plays an important part in the efficiency of working and should receive due consideration. Several kinds of oil have been suggested as suitable for use in the stripping of gas, the chief of which are :—

Moderately light creosote oil.
Heavy creosote oil.
Strained anthracene oil (green oil).
Petroleum distillate (gas oil).
Shale oil distillate.
Blast-furnace oil.

Although the shale oil distillate and petroleum distillate (gas oil) possess good benzene and toluene absorbing powers, they have not received general acceptance, chiefly on account of the risk there is of obtaining a crude benzole containing paraffinoid bodies. A crude benzole containing these bodies is not so valuable on the market on account of the difficulty, and in some cases the impossibility, in separating the paraffinoid hydrocarbons from the rectified products. The fact that gas oil is free from naphthalene and is an excellent solvent for this substance is certainly in its favour. At the time of writing it is being used at some works with good results, but in these cases it is undoubtedly a well-chosen oil. If a petroleum distillate which on distillation yields nothing below, say, 170° C. is employed, the risk of obtaining rectified products containing paraffinoid bodies is much reduced, and with careful working up of the crude benzole satisfactory results may be obtained. When, however, oils of a different class (*e.g.* creosote oils) which introduce no risks of this kind can be easily secured, then it is wise to use them and to avoid paraffin oils.

In regard to the creosotes and strained anthracene oil, these materials seem to be in greatest favour and are used very largely, particularly the heavy creosote. It appears that a coal-tar creosote boiling between 220° and 265° C. extracts benzole and toluole from coal gas better than the heavier coal-tar distillates, but this is not the only factor in the case. Consideration must be given to the amount of wash oil (creosote) which will come over with the crude benzole during the debenzolising process. Using a creosote with a low distilling range will result in a larger amount of its lower boiling-point compounds distilling over with the crude benzole than if a creosote of a higher distilling range be employed. In this respect it is an advantage to use one possessing a distilling range, say, between 250° and 325° C., although the benzole-toluole absorbing power is not quite so great. However, a creosote of this distilling range has one disadvantage, and that is its rather high viscosity when compared with lighter fractions. This results in rather a lower efficiency in regard to its stripping powers, especially during the cold weather, and it also renders the oil a little more difficult to cool after leaving the still. Bearing all these facts in mind, and with a desire to secure as high an efficiency as possible, it is best to use a creosote with a medium distilling range and to employ careful dephlegmation to separate from the crude benzole, immediately it leaves the still, as much as possible of the wash oil which is carried over. One of the best specifications of a creosote for gas stripping which has come to the author's notice is that given by Walmsley and Morfey. This has been referred to in Chapter XX, page 344, but for the sake of convenience the distilling range is given here. It is :—

Dropping point	210°–220° C.
50 per cent. distils over at	250° C.
80 ,, ,, ,,	300° C.

Although the distilling range of strained oil (green oil) is high, it is not so suitable as heavy creosote on account of its high viscosity and its low benzole-toluole absorbing property. A strained oil having a specific gravity of 1·100, on distillation in a Wurtz flask, the thermometer being in the vapour, bulb opposite the outlet, showed—

Up to 220° C.	9 per cent.
,, 240° C.	14 ,,
,, 260° C.	18 ,,
,, 280° C.	28 ,,
,, 300° C.	40 ,,

Further specifications of creosotes used in the process of gas stripping are as follows :—

(*a*)[1] Specific gravity at 60° F.	1·040
Tar acids	8 per cent.
Distilling up to 200° C.	0 ,,
,, ,, 220° C.	20 ,,
,, ,, 240° C.	35 ,,
,, ,, 260° C.	65 ,,
,, ,, 280° C.	75 ,,
,, ,, 300° C.	85 ,,

(*b*)[2] Specific gravity	1·037
Naphthalene	21·6 per cent.
Below 200° C.	0·5 ,,
,, 220° C.	16·5 ,,
,, 240° C.	40·5 ,,
,, 260° C.	61·0 ,,
,, 280° C.	70·0 ,,
,, 300° C.	78·0 ,,

It will be observed that in the last specification the content of naphthalene is high, particularly for a wash oil. The naphthalene trouble is the gasworks managers' "nightmare," and any means by which this trouble can be reduced is always welcome. In the process of stripping gas the content of naphthalene in the gas is usually reduced by the solvent action of the wash oil, but if a wash oil is employed which contains an excess of naphthalene the opposite result will, in all probability, be obtained, particularly if the percentage of napthalene in the gas, before washing, is low. It is desirable on this account to begin with a fresh wash oil practically free from naphthalene and to see to it that that which is picked up from the gas is removed during the debenzolising process by dephlegmation, or else allowed to crystallise out of the debenzolised oil by chilling and settling in suitable tanks.

That washing the gas with oil removes much of the naphthalene should be a strong recommendation to gas engineers to instal a stripping plant, but in doing so they must not lose sight of the fact that the wash oil removes from the gas much of the material (benzene, toluene and xylene) which holds naphthalene in suspension, and that any naphthalene which still remains in the gas may deposit somewhere and cause trouble. This may be prevented by spraying into the gas (after it has been stripped) a suitable solvent by one of the well-known processes, and by doing this the gas will also be enriched.

During the year 1917 blast-furnace creosote received attention in connection with its suitability as a gas-stripping material. It possesses the following advantages :

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[1] *The Gas Chemists Summary*, 1915, p. 82.

[2] "Effect of the War on Gasworks Practice," J. Weyman, M.Sc See *Gas World*, May 13th, 1916, p. 445.

1. The naphthalene content is practically nil.
2. It is a good solvent for benzenoid hydrocarbons.
3. It is an excellent solvent for naphthalene, much better than coal-tar creosotes.
4. It has a high distilling range. There is one disadvantage, and that is during the cold weather it is liable to become more viscid than a suitable coal-tar creosote, with the results mentioned on page 361.

Unfortunately, the volume produced annually is much less than that of coal-tar creosote, and this limits its use. It can, however, be mixed with the coal-tar product with advantage. Owing to the high germicidal value of the tar acids contained in blast-furnace creosote it is much sought after by disinfectant manufacturers, who extract all or most of the tar acids, and who are generally in a position to supply the extracted oil in a condition eminently suitable for gas stripping. A specification of a blast-furnace oil is given by Geoffrey Weyman,[1] which is as follows :

Specific gravity	0·957
Naphthalene	trace
Below 200° C.	4 per cent.
,, 220° C.	7 ,,
,, 240° C.	24 ,,
,, 260° C.	40 ,,
,, 280° C.	58 ,,
,, 300° C.	72 ,,

Some particulars of blast-furnace oils which have been recommended for gas stripping are given in Table 71.

TABLE 71

Sp. Gr. at 15° C.	Tar Acids per cent.	Water per cent.	Per cent. up to						
			220° C.	240° C.	260° C.	280° C.	300° C.	340° C.	360° C.
0·961	5·0	0·5	3	7	20	43	55	80	89
0·960	4·6	trace	3	8	23	42	56	79	86
0·961	4·0	0·5	2	6	24	44	62	81	89

The point as to whether it is an advantage to use a wash oil containing tar acids or not remains as yet unsettled. It is an established fact that tar acids are excellent solvents for naphthalene, while coal-tar hydrocarbons are very poor in this respect. This fact alone seems to decide in favour of using wash oils of the coal-tar creosote type which contain tar acids. These remarks do not apply to blast-furnace oil (tar acid free) as the hydrocarbons contained in it are excellent naphthalene solvents. To illustrate these facts the author gives the following figures, Table 72, obtained by him some time ago under strictly comparable conditions. In the table the solvent power of tar acids extracted from coal tar creosote is taken as 100.

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[1] "Effects of the War on Gasworks Practice." See *Gas World*, May 13th, 1916, p. 445.

In the Brageat process for gas stripping a mixture of cresols is used which boils at 185°–203° C., and which is liquid at a temperature of –18° C. It is said that the amount of liquid to be debenzolised is much less than is usual with other wash oils, as the cresol mixture will absorb approximately three times as much benzole as will creosote oil.

The effect of water in the wash oil on its extractive power is one which requires careful consideration. Practice has shown that as the percentage of water in a wash oil rises, so does its absorptive (or extractive) power decrease. For instance, an oil containing about 3 per cent. of water will absorb approximately 36 per cent. less benzenoid hydrocarbons than a water-free oil, while one containing 7 per cent. will absorb 45 per cent. less. When purchasing an oil for gas stripping it should be laid down that it must not show more than 0·5 per cent. of water when submitted to a distillation test. It must not be forgotten that there are other channels by which water may get into the wash oil. For instance, the gas carries a certain amount of water in the form of vapour, which, if the wash oil is at a lower temperature than the gas, will be taken up by it. It is necessary on this account to see that the wash oil as it enters the washer is at a slightly higher temperature than the gas, say, about 2° C. Water may also get into the oil during its treatment in the debenzolising still if this piece of apparatus is steam heated. As already mentioned, steam-heated stills are fitted with " live " as well as closed steam coils, and if the steam is wet, that which leaves the open steam coil will deposit water in the oil, particularly if the oil, as it enters the still, is at too low a temperature. To avoid this it is wise to superheat the steam a little or pass it through a water separator before allowing it to enter the still. If the benzolised oil is too low in temperature when it enters the still it may bring about condensation of the " live " steam, even when this is supplied in a comparatively dry state. To steer clear of this the temperature at which the benzolised oil enters the still and that at which the debenzolised oil leaves it must be properly controlled. The temperature at both these points should be at least 10° C. above the boiling-point of water, being a few degrees lower at the outlet than at the inlet. Various temperatures have been recommended from time to time, but in the opinion of the writer an inlet temperature of 120° C. and an outlet temperature of 110° C. will, in most cases, give satisfactory results. It must be borne in mind the temperature that the higher used in the still the greater the

TABLE 72

Material.	Naphthalene solvent power.
Coal-tar acids from creosote	100·0
Creosote oil containing 25 per cent. tar acid	26·5
Creosote oil free from tar acids	10·2
Blast-furnace oil free from tar acids	108·9

possibility of forming decomposition products in the oil, and thus hastening its "thickening" and the shortening of time of service of all or part of it. Thickening of the oil is also brought about by the loss of the lighter portions during steam distillation in the debenzolising still, and in some cases by the tar which it picks up from the gas, when the gas is not quite tar free.

It is convenient at this point to mention again that the steam supplied to the still should be dry, and, with advantage, slightly superheated. That which passes through the closed coil, which is fitted in some of the debenzolising stills, will give good results if it is at a pressure of between 60 ℔s. and 80 ℔s. to the square inch. With regard to the "live" steam which enters the still via the perforated coil or steam jets, this must not be introduced at too high a pressure, or some of the unfractionated oil will be blown over with the crude benzole. On the other hand, steam supplied at too low a pressure will not properly fractionate the oil, because as it meets the descending oil at each plate its temperature and pressure fall until finally it reaches a stage, near the top plates, at which it cannot sufficiently agitate and heat the oil nor "lift" the crude benzole vapours to the vapour pipe. Further, steam at very low pressures, unless superheated near the still, is very liable to be wet, and this, in addition to a fall of pressure due to the expansion in the still, will introduce the risk of some water being deposited in the oil. Steam is always reduced in pressure by throttling or wire drawing, and this process takes place when the steam passes the control valve and also when it leaves the perforations in the coil or jets. Hence a supply from a boiler at a very low pressure would be reduced further on entering the still, and in spite of the fact now to be mentioned it is not an advantage in this case. When steam is throttled or wire drawn it is rendered less wet than it was originally, and, in fact, if it is not inordinately wet it is dried and possibly superheated (this is not the case if the pressure is reduced by expansion). It follows from what has been said that steam should be supplied from a boiler working at a good pressure, say, between 60 ℔s. and 80 ℔s. to the square inch; it must be dry; and it should enter the still immediately after being reduced in pressure by throttling with the control valve near the steam inlet. This valve can be carefully opened by the plant man and the supply of steam into the still regulated according to the flow of condensate from the worm end.

The benzenoid hydrocarbons exist in coal gas in the form of vapours, or for all practical purposes in the form of gases; liquids when converted into vapours obey all the laws of gases. In the process under consideration we may consider these bodies as indifferent gases when compared with the solvents used to extract them. The removal of active gases, *i.e.* those which will react easily with an absorbing medium, is a simple matter compared with that of the absorption of indifferent gases. In the former case chemical absorption can be brought about by the employment of a suitable absorbing medium and making use of the ionic state, but in the latter case, having non-electrolytes to deal with both in regard to the gases and the absorbing medium, it is not possible to take advantage of an ionic state, and the process will proceed much more slowly. Bearing in mind the law which governs the solution of gases in liquids, viz., "given a state of equilibrium, the concentration of a gas bears a constant relation to that of the solution," the term concentration indicating the amount present in a unit volume, we shall be able, briefly, to consider the theoretical side of gas stripping. Now, the concentration of a gas and the quantity of it which can be dissolved in a liquid are proportional to the pressure and, naturally, to the nature of the substance used as a solvent. Also, the temperature of both the solvent and the gas will exert their influence.

In the process under consideration the separation by absorption of gases (vapours) of a similar nature, *i.e.* the lower benzenoid hydrocarbons, from a mixture of dissimilar gases is aimed at, and the following points should be borne in mind. The unabsorbed gases (vapours) will carry away with them a certain amount of the material used as the solvent, this amount varying according to the vapour pressures. In any case it is not very considerable. It is necessary to use the *counter current* system of washing ; to expose the largest possible reaction surface in regard to the gas and the solvent, together with sufficient time of contact ; and to maintain a high degree of agitation of the absorbing liquid (the wash oil). The reasons are as follows : As the absorption of the vapours of the benzenoid hydrocarbons goes on their partial pressures in the gaseous mixture becomes less, and the vapour pressures exerted by the benzene and its homologues in the wash oil increases. It is therefore necessary in order to obtain the greatest possible absorption to bring the strongest solution (partly benzolised oil) into contact with fresh or unwashed gas, and fresh wash oil containing as little benzene as possible into contact with partially washed gas. This can be done only by using the *counter current* system. The larger the reaction surface in the washer combined with a properly regulated supply of wash oil the greater will be the surface of contact between the gas and the solvent, the latter being spread out in thin films and the former well broken up into separate currents. A high interfacial area between the gas and wash oil can be obtained by converting the latter into a fine spray. Now the greater the surface of contact, combined with a reasonable limit of time for action, the more efficient will be the absorption of the hydrocarbons by the wash oil. If the wash oil is agitated it is broken up into drops, and the smaller these drops the greater the surface of contact. Agitation is also necessary in order to assist in the dissemination of the dissolved gases throughout the wash oil. Agitation is obtained mechanically, *e.g.* by the use of the Walker purifying apparatus, or the Blair centrifugal scrubber, or by force of gravity, *e.g.* in falling from one board to another as in the board-packed washers. This method, however, does not tend towards the highest efficiency.

The amount of wash oil in circulation has an important bearing on the efficiency of the plant, and it should be carefully controlled after a decision has been come to as to the best volume to use. On plants in various parts of the country the amount of wash oil used varies between 55 and 120 gallons per ton of coal carbonised. The volume should differ according to the degree of saturation aimed at, and this in its turn depends upon the efficiency of the washer and the time of contact between the gas and the wash oil. A good average is between 65 and 70 gallons of wash oil per ton of coal carbonised, and the degree of saturation about 4·5 per cent. If it is assumed that each ton of coal carbonised yields 3 gallons of benzenoid hydrocarbons and a degree of saturation of 4·5 per cent. is aimed at, then 67 gallons of wash oil per ton of coal carbonised will be required. On the same assumption, for a 4 per cent. saturation 75 gallons of wash oil will be required, and for a 3 per cent. saturation 100 gallons of wash oil. In the case of small works, where necessity requires that the benzolised oil be sold or returned to a larger works, then a degree of saturation as high as 9 per cent. is often aimed at. It is interesting to note that experience has shown that below a certain point the smaller the volume of wash oil used per ton of coal carbonised the greater is the amount of toluene and its higher homologues and the less the amount of benzene removed from the gas.

The supply of wash oil to the washer should be regular and at a constant head. If these conditions are varied from the correct standard found for the plant then there is a risk of the gas not being properly stripped or of the wash oil not being kept up to the required degree of saturation. A diminished head or supply may result in the boards, or other material providing the reaction surface, not being properly covered, and an increased head or supply will result in thicker films of wash oil and, therefore, a reduced contact surface.

Reference to the amount of reaction surface required in gas stripping is made on page 351. Satisfactory results will not be obtained if the figures there given are reduced to any great extent—in fact, it would in many cases be advantageous to increase them somewhat, say, for instance, to 20 cubic feet of tower space per ton of coal carbonised per day, representing approximately 620 square feet of reaction surface, if boards are used. These and the figures already given (page 351) are only approximate, and when a new plant is to be erected the type of washer to be adopted and also the extent to which the gas is to be stripped must be considered.

One of the most important factors governing the successful recovery of the benzene hydrocarbons from gas is that of temperature. The temperature of both the wash oil and the gas to be stripped must be carefully controlled. If the temperature of the wash oil is too high when compared with that of the gas, then there is a risk of naphthalene being taken up from the former (in cases in which the percentage is fairly high) by the latter, and also with this same condition of temperature less benzenoid hydrocarbons will be extracted. It is necessary, however, for the wash oil to be at a slightly higher temperature than the gas in order to prevent water being deposited in the oil; this difference should be about 2° C. Good results can be obtained by keeping the gas at about 18° C. and the wash oil at about 20° C. E. W. Smith[1] recommends that the temperature of the wash oil should not be higher than 22° C. in order to secure the best working results.

It may be as well to mention in this place that it is advisable to remove the ammonia from the gas before passing it along to the stripping plant. If this is not done then there is, naturally, some loss of ammonia due to the deposition of ammonium salts in parts of the plant, also there is the risk of increasing the corrosion of some of the units of the plant by certain of the ammonium salts, for instance ammonium chloride, and the reducing of the absorbing power of the wash oil.

During each cycle the volume of the wash oil is reduced by a small amount.

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[1] See *Gas World*, December 16th, 1916, p. 541.

This is mainly due to the fact that some of the lower boiling constituents of the oil are carried over with the crude spirit during the debenzolising process. This amount should be replaced each day by fresh wash oil. It is also necessary to do this to reduce to a certain extent the "thickening" of the oil. Eventually, however, the oil becomes "thick" (*i.e.* the specific gravity, viscosity, and drop point of the oil become higher), and its power of absorbing benzenoid hydrocarbons is reduced. On this account it is put out of commission and a new lot of wash oil supplied to the plant. The "thickening" of the wash oil can be stayed for a considerable period if a certain proportion is removed each week and replaced by fresh wash oil. In this connection E. W. Smith[1] recommends the removal of 10 per cent. of wash oil from circulation per week when using 50 to 70 gallons per ton of coal carbonised. It is advantageous occasionally to add fresh wash oil somewhat lighter in specific gravity to the original, but before doing this the debenzolised wash oil in circulation should be examined in the chemical laboratory for its physical constants.

Care must be taken that the debenzolising of the wash oil is properly carried out before returning it to the washers. A partly debenzolised oil will not absorb the desired amount of benzenoid hydrocarbons, and on this account the efficiency of the stripping plant will be reduced. The oil as it leaves the still should be examined periodically in the chemical laboratory.

Another factor upon which the efficiency of a stripping plant depends is an adequate supply of cooling water for the condenser attached to the debenzolising still (also for the condenser of the rectifying still if this is attached to the plant), and also for the water condenser through which the debenzolised oil passes before entering the storage tanks or receivers. In the case of the debenzolising still condenser a flow of about 2½ gallons of cooling water for each 1 gallon of distillate condensed is a suitable figure to work upon, and for a rectifying still condenser 3 gallons for each 1 gallon of distillate. For the debenzolised oil coolers an allowance of, say, 1½ gallons of water per square foot of condensing surface per hour will prove suitable under most circumstances. A useful and usually safe allowance to make in calculations connected with condensing surfaces for this purpose is 1,000 B.Th.U. per square foot per hour, these units being carried away by the cooling water.

When distilling the benzolised oil (*i.e.* removing the benzenoid hydrocarbons) care must be taken to see that the temperature of the benzolised oil at the inlet and that of the debenzolised oil at the outlet are properly controlled. The correct temperatures to use and the reasons for their employment have already been given on page 364. If the number of compartments or segments in the still is insufficient, then the oil under treatment will leave the still too soon and consequently will not be properly debenzolised. This bad result will also occur if the design of the plates of the segments is faulty, or if the oil is passed at varying speeds through the still. A constant speed must be arranged for. If the oil is supplied to the still in too great a volume, then a choking of the compartments will take place (even when properly designed overflows are provided), and there is a likelihood of benzolised wash oil being carried over with the steam and crude benzole vapours. The most

[1] See *Gas World*, December 16th, 1916, p. 541.

suitable speed at which the oil should travel through the still of any individual plant can be found by examining the wash oil, as it leaves the still, for its content of benzenoid hydrocarbons. When this speed is found laboratory control must not be discontinued, but a daily test carried out on a bulk sample made up of samples collected by the plant man, say, every two or three hours. The debenzolised oil as it leaves the still when submitted to a distillation test in the chemical laboratory should not yield more than, say, 0·3 per cent. up to 160° C.

On page 355 mention was made of the use of a dephlegmator for the purpose of facilitating the removal of much of the naphthalene contained in the debenzolised oil, some of which was possibly in the fresh wash oil and much of which has been taken up from the gas. The temperature at which the vapours leave the outlet of the dephlegmator must be taken from time to time and kept under control, and although a certain amount of latitude can be allowed, any variation must be made with an object in view and not carelessly. For instance,the temperature must be varied according to the "strength" at which it is desired to produce the crude benzole or the percentage of saturation of the benzolised oil. Temperatures between 90° and 95° C. are used with good results, but it is wise for the manager to adjust his own temperature according to conditions obtaining in his particular case. If the dephlegmator is used properly the naphthalene trouble will be considerably reduced, if not wholly done away with.

For the purpose of recovering benzole from gas H. E. Copp[1] suggests that a continuous-process benzole plant be situated at the inlet to the purifiers and should consist of a scrubber, heat exchangers, oil superheaters, crude benzole still heated by live steam, an analyser, main condenser, separator, and oil coolers. Creosote is proposed as the wash oil, which can be prepared in a tar dehydration plant situated alongside the benzole plant. When first prepared the creosote will contain 20 to 25 per cent. of naphthalene and should give the following fractions on distillation :—

up to 200° C.	8 per cent.
200° to 230° C.	32 ,, ,,
230° to 280° C.	20 ,, ,,
280° to 300° C.	15 ,, ,,
residue	15 ,, ,,

On emerging from the scrubber this creosote will contain 2·0 per cent. of benzene hydrocarbons, and after passing through the debenzolising still will retain 0·5 per cent. of benzole. With the object of freeing the creosote from naphthalene, in order that it may wash all the naphthalene out of the gas, Copp inserts a small supplementary condenser or analyser between the still and the main condenser, and this is maintained at a temperature varying between 92° and 98° C., the usual temperature being 96° C. The condensate at this point will consist chiefly of water and naphthalene, which are collected separately. In actual practice the analyser reduces the naphthalene content of the creosote to 6 per cent. with the result that the gas, after scrubbing, is entirely free from the former material. At the inlet to the scrubber the gas contains on an average 16·8 grains of naphthalene per 100 cubic feet, and this is reduced by the wash oil to nil.

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[1] Mid. Assn. Gas Eng. & Managers, October 31st, 1918. *Gas Jour.*, 1918, 311–313.

A. Hartmann[1] advocates the debenzolising of wash oil under vacuum, heating the oil by means of indirect steam at the ordinary pressure.

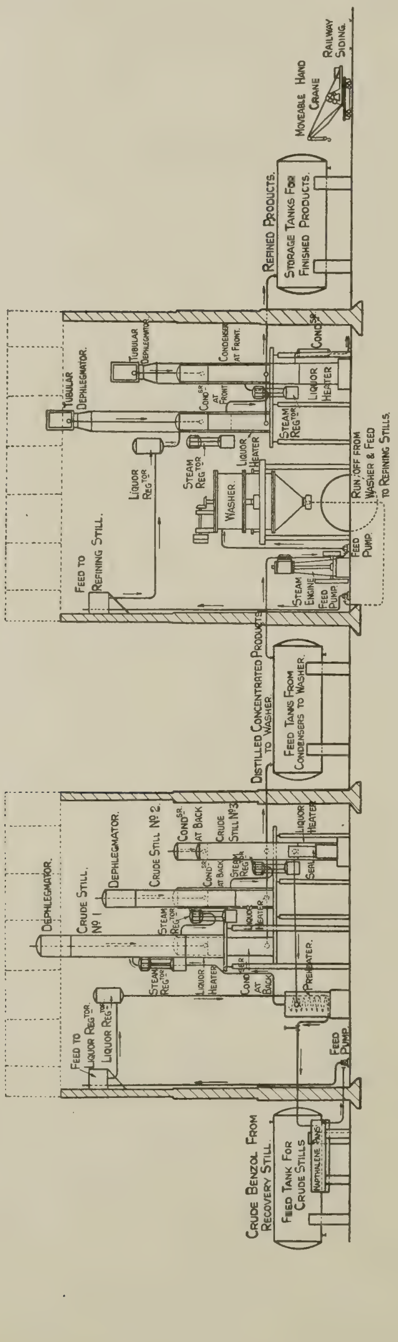

Fig. 123.—Blair's Continuous Benzole Distillation and Refining Plant.

Various grades of crude benzole are made on recovery plants, and some of these are 65 per cent., 60 per cent., and 55 per cent., these percentages representing the amount of distillate which comes over up to 120° C. when 100 c.c. are distilled in a glass retort with the thermometer immersed in the liquid.

The composition of the crude benzole will vary a good deal according to the "strength" or the percentage it gives up to 120° C. on distillation; the quality of the wash oil used; the degree of saturation of the wash oil, and so on; in fact, it is questionable whether two lots will be found alike. In a recent paper[2] Weyman gives the following figures: Benzole, about 55 per cent.; toluole, 9 per cent.; solvent naphtha, 10 per cent.; bottoms, 26 per cent.

With regard to the distillation of the crude benzole, and the rectification of the products, methods and plant for doing this are described in Chapters XII, XIII, and XIV.

Fig. 123 shows the arrangement of a continuous benzole distillation and refining plant by Blair, Campbell, and McLean. The diagram is practically self-explanatory, but the following brief description of the plant and the progress of the material through it will, no doubt, be useful to the reader.

The crude benzole from the debenzolising plant is pumped from its storage tank to an elevated feed tank. From this it flows via a regulator (marked liquor regulator in the diagram) to a preheater. In this piece of apparatus the outgoing residue ("creosote oil ") from crude still No. 3 gives up most of its heat to the crude benzole. From the preheater the heated crude benzole is fed into crude still No. 1, on the top of which is fitted a special type of vertical dephlegmator. It should be noted here that if it is desired to use the plant for the treatment of benzoles of varied compositions, that special arrangements are made to distribute them to the column, or still, at various heights. The crude benzole whilst descending via the trays of the first column (crude still No. 1) exerts a thorough washing of the ascending vapours, and this fact bears great influence on the production of the 90–95's crude product. As the crude benzole flows from the bottom tray it runs into a heating apparatus (liquor heater) and here the benzole is volatilised, and the vapours ascending the column, pass, via the dephlegmator, to the condenser in which they are condensed, and the condensate then flows to a storage tank (feed tank from condenser to washer). The amount of steam which enters No. 1 crude still is very small and it is regulated by a steam regulator, an appliance which is fitted to each of the stills included in this plant, and one which is absolutely necessary for its smooth working.

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[1] Ger. Pat. 298,823, November 14th, 1913.

[2] "The Effect of the War on Gasworks Practice," Geoffrey Weyman, M.Sc. See *Gas World*, May 13th, 1916, p. 444.

The heavy residue from the bottom of No. 1 crude still is led into crude still No. 2 and undergoes a similar treatment to that described in connection with the first still, resulting in the volatilisation of crude 90–95 per cent. toluole, which is finally condensed and run to a storage tank. A similar process takes place in the crude still No. 3, but crude solvent naphtha is distilled off from the bottom of No. 3 still in this case. The residue from crude still No. 3, called creosote oil, passes from the still into a seal pot and from this appliance flows to the preheater. On leaving the preheater it is led to the naphthalene pans in which salting out is allowed to take place.

When sufficient of the crude 90–95's benzole, 90–95's toluole, and solvent naphtha have accumulated, they are submitted in turn to washing operations and fractionations in the refining plant. The washings are carried out in the usual manner as described in Chapter XIII, and the washed product run into an underground feed tank. From this tank it is continuously pumped into an overhead feed tank which distributes it via a regulator (" liquor " regulator) to the first rectifying still. This still has a tubular dephlegmator of the horizontal type fitted on top, which is provided with special facilities for cleaning the tubes, distributing the water, and taking away the condensate.

In the case of washed crude benzole the fore-runnings are taken off in the first still and the residue transferred to the second still. Here the refined benzole is distilled off and a small amount of toluole residue left, which is cooled by means of water, and then fed to a small receiver which is directly connected to the feed pump of the main plant. By this arrangement it can be pumped, along with a crude toluole charge, to the first rectifying still.

Dealing with crude toluole, this, after washing, is passed on to the first rectifying still in which a small quantity of benzole is taken off, and then to the second still which distils off rectified toluole. Any residue is dealt with in a charge of washed crude solvent naphtha. This material is dealt with in a similar manner, yielding a fore-runnings of toluole and solvent naphtha of a quality desired by the management. The residue can be sold as a medium heavy naphtha, or dealt with in any other manner which occasion may require.

An excellent paper, one might almost say a classical paper, on " Some Physico-Chemical Considerations on Benzol Recovery from Coal Gas," has been published by Mr. T. F. E. Rhead, M.Sc.,[1] and the author recommends all those interested in the important subject of benzole recovery to give this paper their careful study. The theoretical principles underlying the process of benzole recovery are dealt with in an excellent manner by Whitehead,[2] and an interesting article dealing with the same subject will be found in the *Gas World.*[3]

In the *Journal of the Society of Chemical Industry* of February 15th, 1917, there occurs a paper by Dr. R. Lessing entitled, " Extracting the Vaporous Constituents from Coal Gas." This communication deals with a suggested method of debenzolising gas by " dry " scrubbing and a method of determining the amount of benzenoid hydrocarbons in coal gas, and it should receive the serious consideration of all who are interested in gas stripping.

The diagram Fig. 124 illustrates the Southport debenzolising plant, which has been erected from material found on the Southport gas estate. Similar material is usually found on most gasworks, or can be readily procured at small cost. The whole of the plant was erected in ten days' time at a cost of £25 (labour only, during the European War), and in working it has given entire satisfaction. The diagram shows the simplicity of the apparatus, and apart from the small amount of labour required on the furnace very little supervision is necessary.

The benzolised oil is continuously pumped into an overhead syphon, which is fitted with an overflow. By the regulation of a cock, marked A on the plan, a regular supply of oil is maintained. The benzolised oil passes through a heat exchanger H, and enters at the bottom of the twin heating tubes at points B. Connected to the inlet pipe there is an extension pipe to the debenzolised oil cooler, which pipe is fitted with a cock, so that at any time the oil can be drained out of the heating tubes, the end flanges removed, and the tubes cleaned when necessary. The oil passes out of the 16-inch heating tubes by means of two 2-inch pipes, at the top of which are mounted thermometers. These thermometers are fixed into the top plugs and made tight by cement. The tubes are connected to the chamber C in the middle of the fractionating column. The benzolised oil, which is heated to a temperature of between 110° and 120° C., passes into the lower portion of the fractionating column through a quantity of steel turnings and rings, as shown in the diagram. At the base of the column there is a small chamber into which a volume of steam is passed. The steam meets the hot oil as it passes through the mass of turnings and rings. It should be noted that the upper portion of the column is filled in a similar manner to the lower portion. By a proper adjustment of the steam a 65 per cent. benzole can readily be obtained from the benzolised oil. It is possible to

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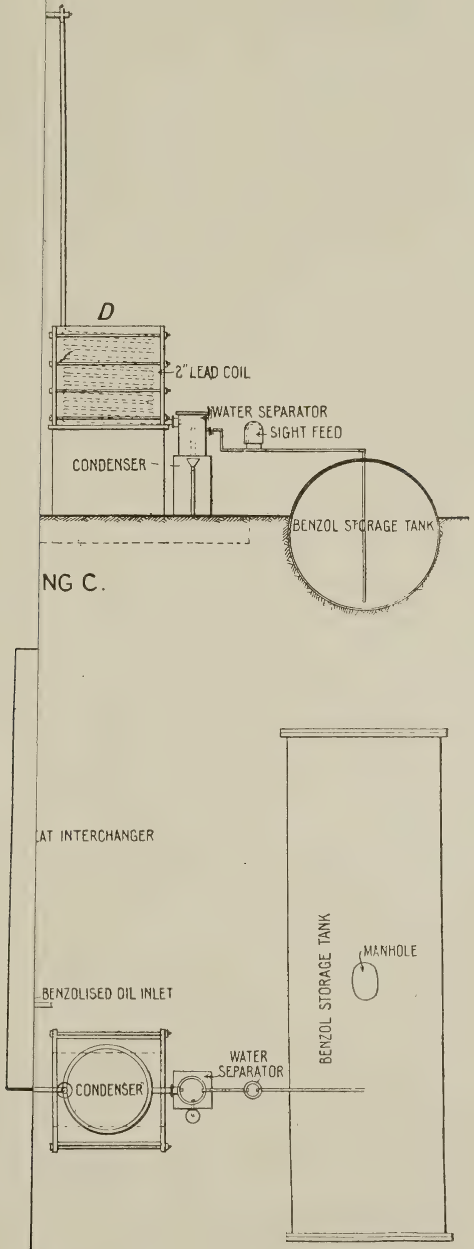
[1] See *Gas World*, January 27th, 1917, pp. 61–66.

[2] " Benzole," Benn Bros., Ltd., London, E.C.4.

[3] *Gas World* (Coking Section), February 3rd, 1923, pp. 16-18.



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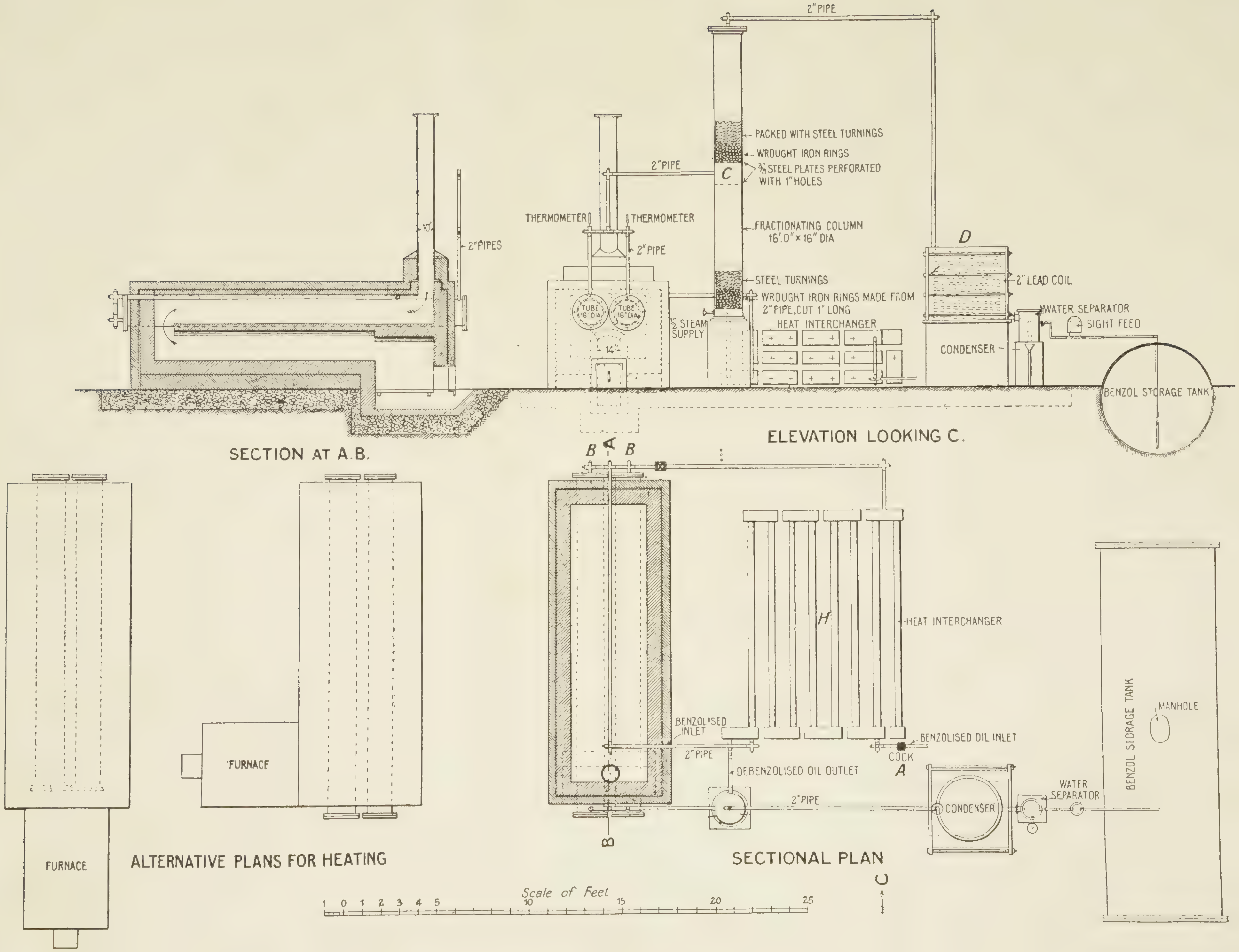

Fig. 124.—The Southport Debenzolising Plant.

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obtain as high as 80 per cent. benzole, but if this quality is maintained a certain amount of benzole returns with the oil to the storage tank.

The benzole condenser D is made from 2-inch lead pipe, and is attached to a small syphon pot at the lower end in which a separation of the water from the benzole is effected.

In the working of the Southport plant the steam is so regulated that the condensed water coming along with the benzole is equal in volume to the crude benzole.

The plant is capable of debenzolising 250 gallons of benzolised oil per hour, and the maximum amount, 264 gallons of 65 per cent. benzole, may be recovered in one day.

A new method of debenzolising gas which by all appearances has a promising future before it, is that of adsorption by silica gel. It is the outcome of research and practical experiment conducted by The Silica Gel Corporation of Baltimore, and the author has to express his thanks to The Kestner Evaporator and Engineering Co., Ltd., of London, England, for particulars of the process and for the use of the diagram from which Fig. 125 was prepared.

The silica gel used in the process is, from a chemical point of view, a hydrated form of pure silica, and as sent out from the factory contains approximately 18 per cent. of water by weight. On exposure to the atmosphere at ordinary temperatures it will either take up or give off water, functions which depend upon the humidity of the atmosphere or the water content of the gel. The name silica gel does not accurately describe the physical nature of the material as used, but rather refers to its condition at one stage of its manufacture. Physically, it is a hard, semi-transparent glassy substance, with the appearance of a clear quartz sand, and a hardness on the mineral scale of approximately five. In structure it is highly porous, and from a great number of observations certain deductions have been drawn which suggest a structure such as would be obtained by piling together, in a uniform manner, spherical particles of extremely small diameter. It is interesting to note that it is possible, by controlling the conditions of manufacture, to produce silica gels of various pore dimensions, and thus obtain materials of different adsorbtive characteristics.

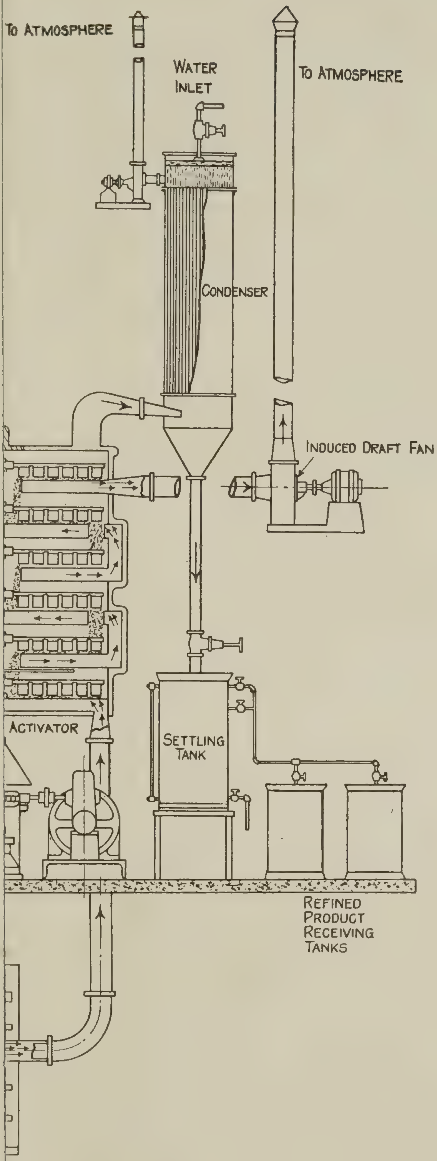
Before the silica gel can be put into use it must be activated, and, in the case of benzole recovery, pulverised. The activation is accomplished by heating to a moderate temperature in a stream of air for a few hours.

In order to debenzolise coal or coke-oven gas the dust type of adsorber plant is used in which pulverised silica gel is employed. The general lay-out of the plant is shown diagrammatically in Fig. 125. Briefly, it consists of three adsorbers in series, each of which is fitted with a dust separator of the cyclone type, and a screw feeder in order to provide for a counter-current passage of silica gel through the system; a screw feeder and discharge fan by means of which the activated silica gel is returned to the adsorption plant; a cooling hopper which is provided with a cold water inlet and outlet, and in which the hot activated gel is cooled before it enters the first adsorber; two automatic bag collectors which are used alternately and in which any silica gel not separated in the second cyclone is removed; an activator of the vertical type; a furnace, the hot gases from which are used to raise the temperature of the activator and to which is connected an induced draught fan; a vertical condenser of the tubular type; a settling tank; and two receivers for benzole. All parts and accessories of the adsorbing equipment and of other portions of the plant are of simple standard types.

The adsorbers contain heat absorbers through which cold water is circulated and by which the heat generated by the process of adsorption is carried away. The coolers are so spaced that the gas will have a low, but ample velocity to carry the silica gel and to insure complete contact between it and the vapour it carries and the gel, and also the heat-transfer surfaces. The silica gel is mixed with the gas in proper proportion and blown through the adsorbing system. Control of the process is maintained by the feeders and inter-stage fans, and not anywhere in the system is the velocity excessive or the pressure more than a few inches water column.

The activator, which deals with the silica gel upon which the benzole is adsorbed, is, as its name implies, the apparatus in which the gel is re-activated, and at the same time a still, for it is here that the benzole and moisture are driven off, and escaping through the swan neck pass to the vertical condenser in which they are condensed. It consists of a vertical cylinder containing a series of hollow shelves which are heated by means of the hot gases from the furnace, as shown in the figure. Through the activator runs a vertical shaft upon which are fitted teeth or ploughs. These are so set that, during the rotation of the shaft, those acting upon the top shelf take the silica gel from the periphery to central openings, and those acting upon the next shelf from the centre to peripheral openings, and so on. On leaving the bottom shelf the hot activated gel travels to a screw feed which returns it to the cycle, via the cooling and storage hopper. The temperature of re-activation approximates 150° C., but it becomes necessary after a time to heat a portion of the gel coming from this activator to a higher temperature. This is due to the fact that traces of high-boiling liquids are not completely removed at the ordinary activating temperature, and therefore accumulate in the pores of the gel, with the result that its adsorptive power is gradually reduced. Activating at a higher temperature is carried out by causing the silica gel to pass through a horizontal rotating activator (not shown in the figure) and submitting it to a temperature of approximately 400°–500° C. This type of activator consists of a rotating steel cylinder with multiple flues and a flue box at either end. It is provided with an axial feed and discharge, for the silica gel and evolved gases, and tumbling shelves on the walls to insure ample contact of the gel with the heating flues. The rotating flue boxes are connected by flexible diaphragms to a fixed combustion chamber or a waste heat source at one end, and at the other to a dust separator and condenser, or a chimney, depending on whether the evolved gas is to be recovered or wasted. This arrangement avoids all difficulties of alignment and leaky stuffing boxes.

It should be noted that the silica gel can be re-activated indefinitely. There is very little mechanical loss of powder (gel), roughly about $\frac{1}{2}$ per cent., and what loss does occur is periodically made up by small additions of fresh gel.



Benzole from Coke-oven Gases.

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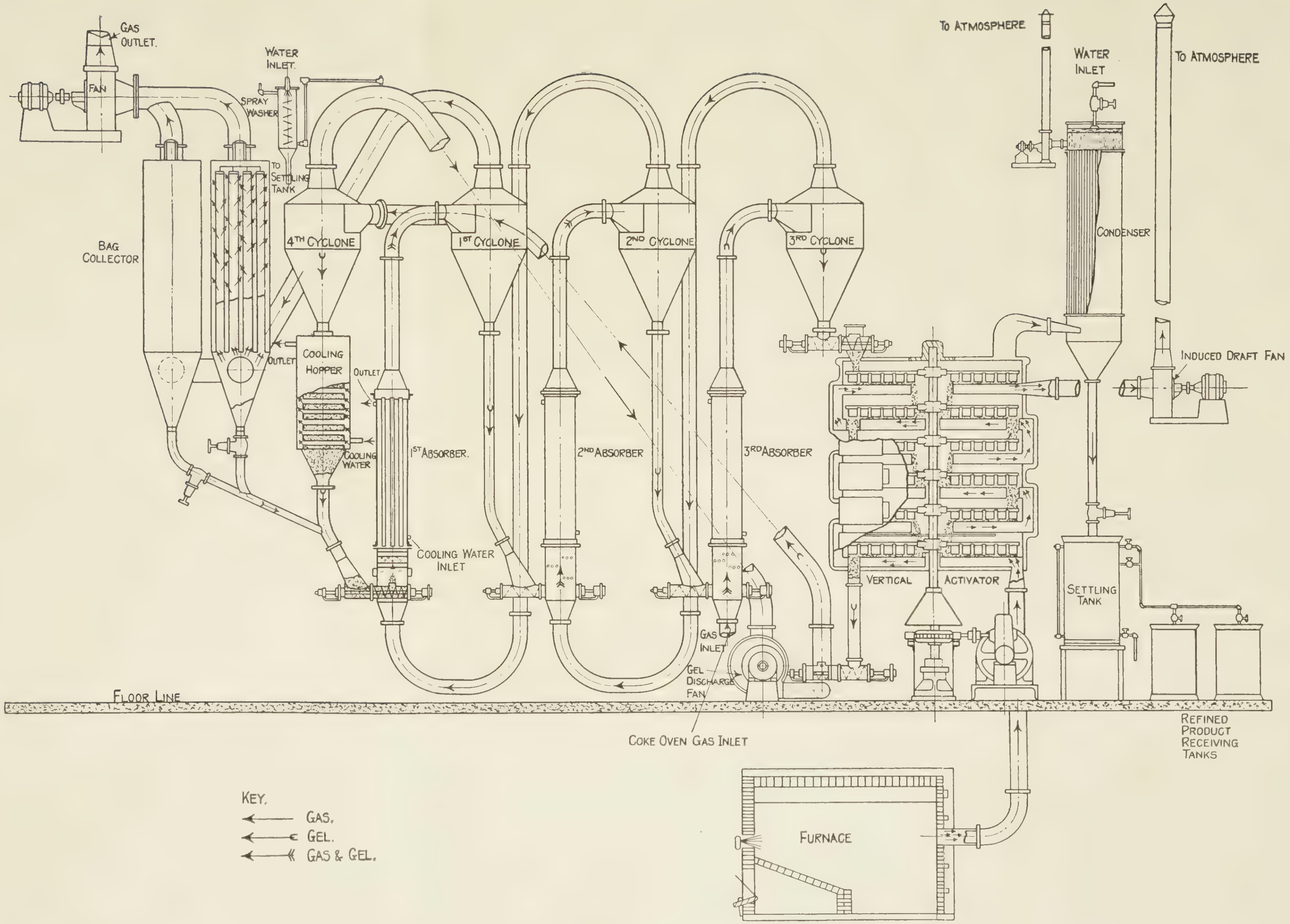

FIG. 125.—DIAGRAMMATIC ARRANGEMENT OF THE SILICA GEL PATENT PROCESS AND PLANT FOR THE RECOVERY OF BENZOLE FROM COKE-OVEN GASES.

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The subject of the recovery of benzole from gas is very thoroughly dealt with by S. E. Whitehead in his excellent work, *Benzol, its Recovery, Rectification, and Uses*,[1] and the interested reader will be well repaid by perusing it.

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Useful papers occur from time to time in *The Gas Journal*, *The Gas World*, and *The Chemical Age* and *Journ. Soc. Chem. Ind.*

[1] Benn Brothers, Ltd., 8 Bouverie Street, London, E.C.4. Price 12*s*. 6*d*. net.

CHAPTER XXII

TARWORKS TESTS

Examination of Tar

Water.—One method of determining this substance in tar is as follows : One hundred grams of tar are weighed into an 8-oz. tubulated retort with a long beak, and 20 to 28 c.c. of benzole added. The lot is mixed together carefully, and the retort is then suspended on a retort stand. A small flame, preferably that obtained with a Rose burner, is placed under it, and the water and benzole which comes over collected in a measure placed under the beak of the retort. The speed of the distillation must be regulated so that the whole of the distillate is condensed. With this method, the water comes over between from $\frac{3}{4}$ of an hour to an hour, without frothing.

Another method which gives excellent and rapid results, but which requires a little more apparatus, is carried out as follows : Into the tubulure of an 8-oz. retort is fitted a funnel sufficiently large to hold 150 grams of tar. The stem of the funnel is shortened and the bore closed by heating in a flame to produce an orifice of about $\frac{1}{32}$ inch in diameter. On the end of a length of glass rod a small piece of india-rubber tubing is placed, and this is inserted into the stem of the funnel, as shown in Fig. 126. A 100 c.c. measure is required to collect the distillate. The retort must have a long beak, or, better, should be connected to a 12-inch Liebig condenser. Into the retort is placed about 50 c.c. of heavy naphtha, free from naphthalene, and 100 grams of tar are weighed into the funnel. The naphtha is now brought to a boil, and immediately the same commences to distil the tar is allowed to run into it through the small orifice in the funnel stem. It will be found that in a few minutes after the tar has left the funnel the whole of the water contained therein has distilled over. With care this operation requires from between 20 minutes to half an hour. S. R. Church recommends the following method : Measure 50 c.c. of coal-tar naphtha, or light oil (which must be free from water), in a 250 c.c. measuring cylinder. Two hundred c.c. of tar are then added and the lot mixed. Transfer the contents of the cylinder to a small copper still, and wash out the cylinder with 50 to 75 c.c. more of naphtha, adding the washings to the contents of the still. The still is connected up to a tube condenser having a water jacket $15\frac{1}{4}$ inches long. Heat is then applied by means of a ring burner and distillation carried on until the thermometer indicates a temperature of 205° C. The distillate is collected in a separatory funnel, into which 15 to 20 c.c. of benzole have been previously placed. The addition of the benzole effects a clean separation of the water from the oil. The water is run off into a measure and the volume read.

Specific Gravity.—Frequently the specific gravity of tar is taken by means of a Twaddell hydrometer. In carrying out the test with this instrument the tar should be brought to 60° F. (15·5° C.). When this temperature is obtained, the hydrometer is carefully placed in the centre of the tar, which is contained in a specific gravity jar, and plenty of time allowed for the hydrometer to sink.

Church recommends the following method for taking the specific gravity of tar : Between 300 to 400 c.c of tar are dried in the same apparatus as used for the water determination, but without the addition of naphtha. The distillation is carried on until a temperature of 170° C. is reached. Any oil which has distilled over is carefully separated from the water and returned to the tar in the still and thoroughly mixed in after cooling. The specific gravity is carried out on this dehydrated tar in a specific gravity bottle of the Hubbard type, whose water capacity at 15·5° C. (60° F.) has been determined by experiment. Ten grams of tar are introduced at a temperature of 40 to 50° C. into the weighing bottle, and the weight taken after cooling. Freshly boiled distilled water is then added, and the bottle kept in a bath at 15·5° C. until no further contraction takes place. The water is then adjusted to the mark, and the bottle removed from the bath and weighed. Weight of tar divided by the weight of the water displaced will give the specific gravity.

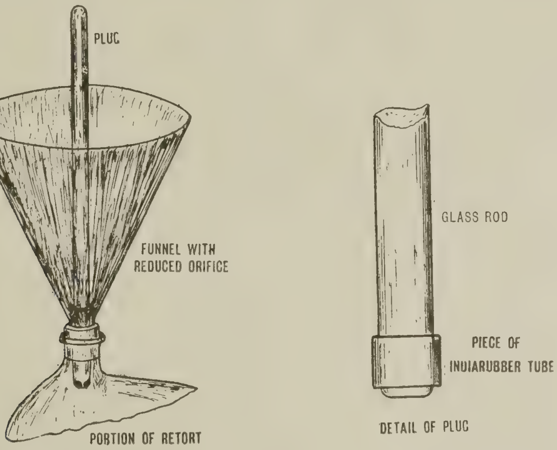

FIG. 126.—FUNNEL AND PLUG USED IN DETERMINING WATER IN TAR.

Another method of taking the specific gravity is to place about 200 c.c. of tar in a large covered beaker and immerse the same in warm water, the temperature of which must not exceed 50° C. This will cause entangled ammoniacal liquor to collect on the top of the tar, when it is removed either by decantation or absorbing it with blotting-paper. A portion of the dehydrated tar is then placed into a specific gravity bottle (Regnault type) and the determination taken at a temperature of 15·5° C.

Lunge estimates the specific gravity of tar by employing a weighing bottle of the shape illustrated in Fig. 127. This bottle is provided with a rill, R, 2 mm. wide. The specific gravity is taken as follows : The weighing bottle is first weighed empty, and then again after filling it with water at 15·5° C. The bottle is then dried, dehydrated tar poured into it until it is about two-thirds full, and the bottle, without its stopper, is then placed into hot water for about an hour, in order to disperse air bubbles. The weighing bottle and contents are then allowed to cool to a temperature of 15·5° C. and weighed. The bottle is now filled with distilled water, the stopper inserted, and any water which issues from the rill is removed, and the whole allowed to stand in a vessel containing water of a temperature of 15·5° C. for about an hour, after which the weight is again determined. The specific gravity is found by the following calculation : (*a*) Equals the weight of the empty bottle ; (*b*) equals the weight of the bottle filled with water ; (*c*) equals the weight of the bottle plus the tar ; (*d*) equals the weight of the bottle, tar and water ; (*s*) equals specific gravity.

$$s=\frac{c-a}{b+c-(a+d)}$$

Free Carbon.—The methods of determining this material are fairly numerous, but the one which in the author's opinion gives the best result is that devised by Hooper. This method unfortunately takes a considerable time to carry out, and on this account the author modified it, and by doing so reduced the time to about one-quarter of that which is required to carry out Hooper's test. The degree of accuracy is in favour of Hooper's test, but in the case of the author's method the amount of error is not a very serious one, and where time is an important matter it may be used. Hooper's test is carried out as follows : 10 grams of tar are weighed into an extraction thimble, which is then closed with a cotton-wool plug and placed into a Soxhlet apparatus. The thimble and plug are previously extracted with the solvents used in the process, dried and weighed. The tar is then extracted with (*a*) 90's benzole, (*b*) 90 per cent. at 140° C. pyridine bases, and (*c*) unmineralised methylated spirit, extracting 50 times with each solvent. The thimble is then removed, dried in a steam oven, and weighed when cold.

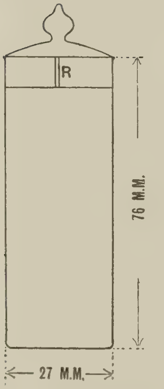

FIG. 127.—SPECIFIC GRAVITY BOTTLE FOR TAR TESTING.

The following is the author's method of determining free carbon in tar ; An extraction thimble, plug of cotton-wool, and lid of filter paper are extracted, first with 98 per cent. cresylic acid, and then with 90's benzole, until extractions are colourless. The lot are then dried and tared. Ten grams of tar are weighed into the thimble, the plug inserted, and the filter-paper cap placed over and held in position with a piece of thin platinum wire. The prepared thimble is then placed in a Soxhlet apparatus and allowed to soak in 90's benzole for a quarter of an hour, after which four extractions with 90's benzole are made. Extraction with 98 per cent. cresylic acid is then commenced, and continued until it runs away colourless, after which 90's benzole is passed through the apparatus until it shows no colour.

The thimble is then removed from the Soxhlet tube, dried in a steam oven and weighed when cold.

S. R. Church has adopted a very compact and simple extraction apparatus (Fig. 128), for use in the estimation of free carbon in tar, which in the author's hands has given excellent results.

"Free Carbon" in Tar

G. S. Munroe and H. J. Broderson[1] found that when tars were left in contact with various solvents for different periods of time the amounts of "free carbon" varied. The method they used to determine the "free carbon" was that of Weiss (*J.S.C.I.*, 1914, 474). The results obtained by these workers showed a gradual increase in the amount of "free carbon" with the time, when benzene, bromo-benzene, and chloroform were used. Other experiments were conducted until the tar was digested with the solvent for definite periods, the water bath being used as the source of heat. The same solvent was used for the extraction, and the insoluble residue left after this process dried and weighed as "free carbon." When benzene was used as the solvent gasworks-tar and water-gas tar yielded amounts of "free carbon" which gradually approached a maximum and then decreased. Similarly, if gasworks tar was subjected to continued digestion with toluene, there was a gradual increase in the "free carbon" content. Curious to relate, if coke-oven tar was treated in the same manner no maximum point was reached. With the solvent chloroform no maximum point was reached in the case of any tar on digestion, but there was a gradual rise in the percentage of "free carbon." It is thought by these workers that fluctuations in the boiling-points of the mixtures during the digestion indicated the probability of chemical reactions taking place, and this seems to apply chiefly to the solvent chloroform. This phenomenon would not account completely for the gradual increase in the "free carbon" obtained on continued digestion. It was found by the authors that carbon disulphide, benzene and toluene do not react chemically with bodies contained in tar, and

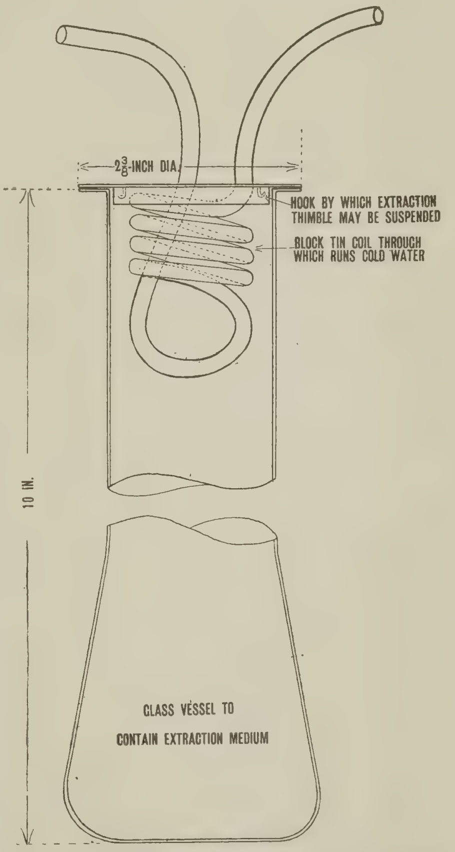
2⅜-INCH DIA.
HOOK BY WHICH EXTRACTION THIMBLE MAY BE SUSPENDED
BLOCK TIN COIL THROUGH WHICH RUNS COLD WATER
10 IN.
GLASS VESSEL TO CONTAIN EXTRACTION MEDIUM

Fig. 128.—Apparatus adopted by Church for the Determination of "Free Carbon" in Tar.

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[1] *Jour. Ind. Eng. Chem.*, 1917, 9, 1100–1101. *J.S.C.I.*, February 28th, 1918, No. 4, p. 84A.

on this account should be used in preference to chloroform for the determination of "free carbon."

A paper by R. Hodurek on the determination of "free carbon" in coal tar and pitch, published in *Mitt. Inst. Kohlenvergasung*, 1919, 1, 9–10, 19–21, 28–30, is worthy of the attention of students. An abstract of this paper will be found in the *Journal of the Society of Chemical Industry*, September 30th, 1920, page 622a.

Sulphur.—It is sometimes desirable to estimate this substance in coal tar, and a good test is recommended by A. Renfred Myhill. A full description of the method is given in *The Gas World* for February 1st, 1913. Briefly, it consists of igniting in a special manner a weighed quantity of tar with anhydrous sodium carbonate in a nickel crucible. After the fusion the mass is lixiviated with distilled water. Any sodium sulphite in solution is oxidised with bromine water and the total sulphate determined by the usual method with barium chloride and the result calculated to sulphur.

The following method for the estimation of sulphur in tar is recommended by P. Falcoila[1] :—0·5 g. of the tar is accurately weighed and intimately mixed by means of two spatulas with about 15 g. of a mixture of four parts of potassium chlorate, one part of ammonium nitrate and one part of potassium nitrate. This mixture is introduced into a test tube, which is then supported vertically in a very tall beaker by means of glass beads. This beaker is then placed in a wider and much taller one. A fuse is brought in contact with the mixture in the test tube, and then ignited. Immediately after this operation the test tube and the beakers which contain it are covered with a heavy glass cylinder, the edges of which are notched with file marks. Into the larger beaker are placed 500 to 600 c.c. of water containing pure sodium hydroxide and a few drops of bromine water. The combustion of the mixture takes some little time, and the gases emitted during this process are washed by the alkaline liquid in the larger beaker. After the combustion is over, the apparatus is allowed to cool, the cylinder removed and washed, and the washings, as well as those from the test tube and glass beads, being added to the liquid contained in the larger beaker. The whole of the liquid is then acidified with hydrochloric acid, concentrated, filtered, and precipitated hot with barium chloride in the usual way. The barium sulphate is filtered off and weighed as usual, and from the weight obtained the amount of sulphur is calculated.

Ash.—This may be carried out by igniting carefully 5 or 10 grams of tar in a large open porcelain or platinum crucible. Every precaution must be taken at the beginning of the operation to avoid frothing over, especially if the tar contains an excess of entangled liquor. Dehydrated tar may be used for the estimation if desired.

Testing Tar for Yield of Products.—Sometimes it is desired to determine in the laboratory the yield of products which may be obtained from a certain sample of coal tar. Laboratory tests for determining the yield of crude naphtha, light oil, creosotes, pitch, etc., are not very satisfactory, and will not give more than an approximate idea of what may be expected in the works. It is far better to erect in the works an experimental still which will deal with, say, 5 cwts. or even a ton, or, better, to work through a charge of, say, 15 or 20 tons of the tar. There are occasions, of course, when this cannot be done, and then at least *two* gallons of tar should be distilled in the laboratory. This may be carried out in a specially made copper still, cylindrical in shape, the diameter being a little less than the height, and provided with a vapour pipe, a safety-valve and a thermometer, using a high-pressure gas burner to supply the heat, and surrounding the still with firebricks. The vapour pipe of the still is connected up to an 18-inch Liebig condenser, through the jacket of which, during the distilling off of the crude naphtha and the first portion of the light-oil fraction, cold water is allowed to flow. After the first portion of the light-oil fraction has come over the jacket is filled with hot water in order to prevent choking with naphthalene salts. The thermometer bulb should be in the vapours and as near the outlet of the vapour pipe as possible. Fractions are collected according to the requirements of the works manager ; in a general way, however, the following may be taken as a guide :—

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[1] *Giorn. Chim. Ind. Applic.*, 1920, 1, 38–45.

Crude naphtha, up to	170° C.
Light oil, between	170–240° C.
Middle oil ,, ...	240–270° C.
Heavy oil ,, ...	270–350° C.
Pitch, above	350° C.

The following table by J. M. Weiss will, no doubt, prove useful to tar works chemists :—

Source of tar.	Free Carbon. per cent.	Specific Gravity at 60° F.	Coefficient of expansion for °F.
Water gas tar . .	1·04	1·073	0·0003750
Water gas tar . .	1·08	1·090	0·0003550
Gasworks coal tar .	16·67	1·203	0·0003125
Gasworks coal tar .	18·53	1·205	0·0003125
Gasworks coal tar .	27·50	1·249	0·0003100
Gasworks coal tar .	33·17	1·296	0·0002700
Coke oven coal tar .	8·97	1·185	0·0003375
Coke oven coal tar .	5·27	1·193	0·0003350
Coke oven coal tar .	4·04	1·178	0·0003300
Coke oven coal tar .	6·72	1·195	0·0003250
Coke oven coal tar .	6·65	1·197	0·0003125
Coke oven coal tar .	9·10	1·203	0·0003125
Coke oven coal tar .	19·06	1·258	0·0003075
Coke oven coal tar .	15·02	1·231	0·0003050

TARS FOR ROAD MAKING

The Ministry of Transport have recently revised the specifications for tars No. 1 and No. 2, and below will be found some of the particulars contained in the booklet which has been issued by H.M. Stationery Office[1] :—

ROADS DEPARTMENT SPECIFICATION

For Tars No. 1 and No. 2

General

1. The tar shall be prepared in stills or dehydrating plant from tar produced in the carbonisation of coal or produced in the use of coal in blast furnaces, except that the tar from which it is prepared may contain not more than 15 per cent. of the tar produced in the manufacture of carburetted water gas.

2. The tar, when tested according to the methods described in Appendix "A," shall conform to the requirements specified under the appropriate heading, viz., 3 (*a*) for Tar No. 1 and 3 (*b*) for Tar No. 2.

4. Schedule of Requirements.

Requirements to be fulfilled on testing.	Specification No.	
	3 (a).	3 (b).
	Tar No. 1.	Tar No. 2.
Specific gravity at 15° C., not higher than	1·225	1·240
Water or Ammoniacal Liquor, not more than	1·0 per cent. by weight.	1·0 per cent. by weight.
Other Distillate (*Light Oils*) *below* 170° C., not more than	1·0 per cent. by weight.	
Distillate between 170° *and* 270° C. (*Middle Oils*), within the range	12·0–24·0 per cent. by weight.	10·0–18·0 per cent. by weight.
Distillate between 270° *and* 300° C. (*Heavy Oils*), within the range	4·0–12·0 per cent. by weight.	6·0–12·0 per cent. by weight.
Phenols or Crude Tar Acids, not more than	5·0 per cent. by volume.	4·0 per cent. by volume.
Naphthalene, not more than	8·0 per cent. by weight.	5·0 per cent. by weight.
"*Free Carbon*," not more than	22·0 per cent. by weight.	24·0 per cent. by weight.
Consistency or *Viscosity*, within the range	3·0–20·0 seconds.	20·0–100·0 seconds.

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[1] "General Directions and Specifications relating to the Tar Treatment of Roads." H.M. Stationery Office, 1923. Price 1*s*. net.

3. Tar for the surface tarring of roads shall fall within the requirements specified under 3 (*a*) for Tar No. 1, and tar for making tar-macadam shall fall within the requirements specified under 3 (*b*) for Tar No. 2, but tars of which the consistency lies between 15 and 25 seconds must not be supplied for either purpose unless specifically allowed by the Surveyor responsible for the work in the terms of the contract or order for the tar. (Tars of which the consistency lies between 15 and 25 seconds usually need special conditions or special experience to ensure good results from them for either purpose.)

Surveyors may also, at their discretion, specify that the tar shall contain not less than 10 per cent. of "free carbon," but this limitation will exclude some tars from Scotch sources and from certain types of carbonising plant elsewhere, which have given satisfactory results in the hands of those accustomed to their use.

Analyst's Report

5. The results of the testing of the sample of tar shall be reported by the analyst on the form of which a specimen is given in Appendix "B."

APPENDIX A

Methods of Testing

1. The methods of testing which shall be used to ascertain if a tar conforms to the requirements of the Roads Department Specification are stated below in so far as they depart from ordinary analytical practice, or need precise definition.

Specific Gravity

2. The specific gravity of the tar at 15° C. may be ascertained by the analyst by any trustworthy method, but for comparative purposes and to check the uniformity of deliveries sufficiently accurate results may be obtained very quickly by the use of Hutchinson's nickel-silver hydrometer, or "tar-gravity gauge," with temperature corrector.

Distillation Test

3. A distillation flask, of a nominal capacity of one litre and without special fractionating column, shall be one-half to two-thirds filled with a weighed quantity of the tar, which shall then be distilled. The flask shall be fitted with a standardised thermometer, graduated in degrees over a range of not less than 80° to 330° C. The top of the bulb of the thermometer shall be level with the lower edge of the opening of the side tube of the flask. The products of distillation up to a temperature of 200° C. shall be condensed by cooling with a cold-water condenser; above that temperature the condenser-tube shall be used without the cold-water jacket.

4. The distillate below 170° C. shall be collected in a weighed measuring cylinder and weighed. The volume of water or ammoniacal liquor shall be read in the cylinder to the nearest half cubic-centimetre, and—taking 1 c.c. of the water or liquor as equal to 1 gram—the percentages by weight of the water or ammoniacal liquor and

of the other distillate (light oils) are calculated. (For Tar No. 2 it is unnecessary to ascertain separately the percentages of water and other distillate.)

5. The distillate between 170° and 270° C. (middle oils) shall be collected in a weighed vessel and weighed, and its percentage by weight calculated. This distillate shall be reserved for the determination of phenols and naphthalene.

6. The distillate between 270° and 300° C. (heavy oils) shall be collected in a weighed vessel and weighed, and its percentage by weight calculated.

7. A valuable check on the result of the distillation is obtained by weighing the flask containing the residual pitch. The total of the weights of all the distillates and of the residual pitch should usually represent not less than 99 per cent. of the weight of tar taken for the distillation.

Phenol

8. The phenols or crude tar acids shall be determined by bringing the whole of the distillate between 170° and 270° C. (middle oils) to a temperature of 40° to 50° C., adding to them about 20 per cent. of solution of caustic soda having a specific gravity of about 1·20, and shaking vigorously every five minutes while keeping the mixture at 40° to 50° C. At the end of 15 minutes the mixture is poured into a tap-funnel, and after the solution of caustic soda has settled out, this solution is run off into a measuring cylinder. The extraction is repeated precisely as before with the same amount of fresh solution of caustic soda, which is separated and run off into the measuring cylinder which contains the first extract. The contents of the measuring cylinder are then made slightly acid by gradual addition of hydrochloric acid. The volume of the phenols or crude tar acids which are thereby liberated is read off, and their percentage on the volume of the tar taken for the distillation is calculated.

Naphthalene

9. To determine the naphthalene, the distillate between 170° and 270° C. (middle oils), after separation of the phenols, is weighed, warmed sufficiently to dissolve all the naphthalene in it, well agitated, and an aliquot part—not less than 25 grams—taken. This aliquot part is cooled to 15° C. and kept at that temperature for half an hour. The naphthalene which has settled out is then filtered off with the aid of a filter pump, and pressed between folds of filter paper until all the oil has been removed by the paper. The naphthalene is then weighed, and its percentage by weight on the tar is calculated.

"Free Carbon"

10. Matter in the tar which is insoluble in benzole of the commercial 90 per cent. grade shall be reported as "free carbon," provided that not more than 10 per cent. of this insoluble matter is retained on a sieve of 80 holes to the linear inch.

11. The determination of "free carbon" may ordinarily be made by either of the three methods described below, but in the event of the result obtained by either of the other methods being above the specified maximum, the determination shall be finally made by the first method, and the result obtained by that method shall be accepted as correct and conclusive. The three methods, if carried out with due

care, should give identical results. Either the first or second method is usually preferred in works laboratories, while the third is specially suitable for laboratories in which it is imperative to avoid the greater fire-risk attendant on the use of a relatively large quantity of benzole. Whichever method is followed, the sample of tar should be thoroughly stirred before the portion for the determination is drawn from it.

(i) *First Method.*—Two grams of the tar is mixed with cold benzole, and after the free carbon has settled out the benzole is decanted off through a balanced pair of filter papers. The free carbon is washed with benzole by decantation several times, and is then passed on to the filter, and washed with 500 c.c. of hot benzole. The total quantity of benzole used in the extraction shall be one litre. The filter papers and contents are dried and the "free carbon" is weighed.

(ii) *Second Method.*—Two grams of the tar is mixed in a small beaker with 25 c.c. of benzole, and the mixture is stirred while it is being heated to boiling. After it has boiled it is filtered through a Gooch crucible prepared in the usual way, and the beaker is washed out repeatedly with hot benzole until all its contents have been thereby transferred to the crucible. Cold benzole is then run slowly from a tap funnel through the crucible until the quantity of benzole used in the extraction amounts in all to one litre. The "free carbon" is dried and weighed.

(iii) *Third Method.*—Between 9 and 11 grams of the tar is mixed in a small beaker with benzole, and the mixture is passed, by repeated washings of the beaker with benzole, into an extraction thimble, previously dried and counterpoised against a dried thimble previously extracted with benzole. The contents of the thimble are then completely extracted with benzole in a Soxhlet or similar apparatus (in which the thimble should not be quite submerged in the benzole), and the thimble is then dried and weighed against the dried counterpoise. The weight of its contents is taken as the weight of "free carbon." The total quantity of benzole used need not exceed 200 c.c.

Consistency

12. The consistency or viscosity is ascertained by the time, stated in seconds, taken by Hutchinson's Tar-Tester or Viscosity Gauge, No. 2 poise, to sink from the lower to the upper ring of the gauge, when it is placed in the tar while the latter is at a uniform temperature of 25° C. and is contained in a vessel of which the internal diameter is between 95 and 102 millimetres (*i.e.* 3¾ and 4 inches).

Sampling

13. A sample of tar for analysis should not be less than half a gallon (and if drawn from barrels should be from a massed sample taken from at least six barrels), and should be in a can or other vessel which, before filling, was both clean and dry inside.

APPENDIX "B"

Specimen of Standard Form on which Analysis of Tar is to be given.

Form No. 152 (Roads)
County................
Reference No. ....

MINISTRY OF TRANSPORT

(Roads Department)

Particulars of Tar, to Roads Department Specification for work of grouting or coating material with tar, in connection with Application for Advances.

1. Origin of Tar (Gas, Coke Oven, or Blast Furnace Works, or Tar Distillery)......
2. Temperature at which Dehydrating Plant is worked........................
3. Proposed use of Tar ; *e.g.* Grouting ; Coating ; or Surface Dressing...........
Particulars of Analysis in accordance with Appendix " A " of Specification.
4. Specific Gravity at 15° C..
5. Water or Ammoniacal Liquor .. Percentage by weight................
6. Other Distillate below 170° C. .. Percentage by weight................
7. Distillate between 170° & 270° C. .. Percentage by weight................
8. Distillate between 270° & 300° C. .. Percentage by weight................
9. Phenols or Crude-Tar-Acids .. Percentage by volume................
10. Naphthalene .. .. Percentage by weight................
11. " Free Carbon " .. .. .. Percentage by weight................
12. Consistency or Viscosity (Hutchinson) at 25° C. .. Seconds................

PITCH TESTS

The usual tests applied to pitch are : (*a*) Determination of twisting-point ; (*b*) ash, and (*c*) volatile matter. Occasionally it is required to estimate the specific gravity and the free carbon.

Specific gravity.—This is estimated by the usual displacement method.

According to H. J. Hailstone,[1] it may be determined by using a solution of sodium thiosulphate of a specific gravity of between 1·2 and 1·35, the method of determination being as follows : 10 c.c. of thiosulphate solution are placed in a beaker and a small pellet of the pitch is then dropped into the solution. Water is then added from a burette until the pellet will remain suspended in the liquid, neither floating nor sinking. The volume of water added is noted, and from a curve which is prepared beforehand the specific gravity is obtained.

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[1] *Gas Jour.*, 1920, 151, 566.

Free Carbon.—The method used for estimating this substance is the same as that employed in the case of coal tar. Of course, it is advisable to grind the pitch to a powder, should the same be hard enough.

Twisting-Point.—There are various ways in which this is carried out, and unfortunately this is the cause of many disputes. In the author's opinion it is far better to rely upon a satisfactory method of estimating the volatile matter in pitch than any method of determining the twist. One method of determining the twist is that of Kohler, which is as follows: Pieces of pitch $\frac{3}{16}$ inch in thickness are placed in water at 60° C., and after this has cooled to 55° C. the pitch should be easily twisted without breaking. Pitches which answer this test are considered suitable for the manufacture of briquettes.

Another method is to take a 1-oz. sample of the pitch, soften it in warm water, and shape it between the fingers until a rod of approximately $\frac{1}{2}$ inch in diameter is formed. This is allowed to harden again, and after an interval of about an hour, when immersed in water at 60° C., it should easily twist. A pitch which answers this test may be employed in the manufacture of briquettes.

Another method which is used to determine the twisting-point of pitch for the manufacture of patent fuels is to immerse a piece of pitch 4 inches long and $\frac{3}{4}$ inch in diameter in water at a temperature of 60° C. for two minutes. After the expiration of this time it should bend without breaking.

A method which is used to determine the twisting-point of any quality of pitch is to take a sample of the pitch, heat it (in water) sufficiently to make it pliable to the fingers, and then form a rod about 2 inches long and $\frac{1}{2}$ inch in diameter. This rod is allowed to harden, and then suspended on a piece of string so that it hangs inside a beaker containing cold water. A thermometer is also suspended inside the beaker, the bulb of which should touch the rod of pitch. The beaker is placed on a piece of wire gauze, and heated with a Rose flame at such a rate that the water increases in temperature 2° F. per minute. It is necessary that the water be stirred very frequently to ensure an even temperature, and the pitch occasionally lifted out and an attempt made to twist it. When it is possible to twist the sample two or three times with only a slight effort the twisting-point is found.

Melting-Point.—To determine this, S. R. Church recommends the following:—

A $\frac{1}{2}$-inch cube of the pitch to be tested is formed in a mould, care being taken not to heat the pitch unduly long or at a higher temperature than necessary. A 600 c.c. beaker is supported on a wire gauze over a Bunsen burner, and hanging into the beaker are a thermometer and a copper wire (No. 12 gauge) hook. The cube of pitch is placed on this hook and suspended in the beaker at such a height that the bottom of the cube is just 1 inch above the bottom of the beaker. Water to the amount of 400 c.c. is placed in the beaker and the temperature brought to 15·5° C., and the pitch is allowed to remain five minutes in this water before heat is applied. The water is to be heated at such a rate that its temperature is raised 5° C. (9° F.) per minute. Immediately the pitch touches the bottom of the beaker the temperature is noted and recorded as the melting-point of the pitch. (To prevent the melted pitch from sticking to the beaker, place a small piece of paper on the bottom and suitably weight it.) This method is employed for pitches which possess a melting-point between 43° and 77° C.

For pitches with a melting-point below 43° C. immerse the cube of pitch in water at a temperature of 4° C. (40° F.) for five minutes before commencing the heating.

If the pitch to be examined melts above 77° C. use cotton-seed oil instead of water, immersing for five minutes at a temperature of 15·5° C. before heat is applied.

Volatile Matter in Pitch.—There are several methods of determining this, and unfortunately there is no standard one. The author made a considerable number of experiments, some little time ago, on the subject of the determination of volatile matter in pitch, and published many of the results in a paper read by him before the Midland Junior Gas Engineering Association.[1] The method which seemed to give the best results is as follows: A porcelain crucible 4 cm. in diameter and 2½ cm. deep, containing 2 grams of ground pitch, is placed in a Leune furnace (such as is supplied with a Meker burner), with the lid on, the top portion of the furnace being removed. A No. 2 size Meker burner is used. The heating is extended over a period of ten minutes, and the flame kept at full blast the whole time. The furnace cover is put on after the first five minutes has elapsed. The crucible, without the lid, is then allowed to cool in a desiccator and weighed, the loss being the volatile matter.

Ash in Pitch.—This may be determined by igniting the residue left after the determination of the volatile matter, or igniting a freshly weighed-up portion. The method of estimation is quite simple and does not need any description.

Standard Pitch for Road Purposes in the United Kingdom[2] shall be specified as under :—

BRITISH STANDARD SPECIFICATION FOR PITCH

General

1. This pitch is suitable for pitch-grouting. See "Road Board General Directions for Pitch-Grouting."

Consistency

2. The pitch is obtained of the required consistency most conveniently by running it off from tar stills in which the distillation of the tar has been stopped at the point at which the residual pitch will give a penetration of 70 (or such other penetration as may be specified to suit climatic or local conditions) when tested at 25° C. (77° F.) on a penetrometer. Harder pitch may be softened or cut back, in the still or in a mixer at the tar works to the extent necessary for it to give this penetration, by the addition of tar oil of the grade specified below in Clauses 7 to 10.

Where pitch of the required consistency is not thus directly procurable, it may be prepared by softening commercial soft pitch, as specified below in Clauses 4 to 6, by the addition of tar oil as specified below in Clauses 7 to 10. In preparing the softened pitch in this manner the tar oil is added to the pitch in the manner described under " Instructions for Melting the Pitch " in the " Road Board General Directions for Surfacing with Pitch-Grouted Macadam," in such proportions that the resultant softened pitch will give a penetration of 70 (or such other penetration as may be specified to suit climatic or local conditions) when tested at 25° C. (77° F.) on a penetrometer, with a No. 2 needle weighted to 100 grams for five seconds.

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[1] "Investigations on Coal Tar and some of its Products." *Transactions of the Junior Gas Association*, 1911–1912. *The Gas World*, March 2nd, 1912, p. 284.

[2] Reprinted by permission of the British Engineering Standards Association from B.S. Specifications for Tar and Pitch for Road Purposes, No. 76–1916, Official copy of which can be obtained from the Secretary of the Association, 28 Victoria Street, Westminster, S.W.1. Price 1*s*. 2*d*. post free.

PREPARED PITCH FROM TAR DISTILLERIES

General Characteristics

3. Pitch which has been procured of the required consistency directly from a tar distillery needs only to be thoroughly melted in the pitch heaters or boilers, but as a precaution against burning, 1 to 2 per cent. of tar oil may advantageously be put into the boilers with the pitch.

Pitch which has been procured of the required consistency directly from a tar distillery shall not yield more than 4 per cent. of distillate below 270° C., or 518° F., on distillation as described below in Clause 5, and shall contain not less than 16 per cent. and not more than 28 per cent. of " free carbon," as defined below in Clause 6.

COMMERCIAL SOFT PITCH

Source of Pitch

4. The pitch shall be derived wholly from tar produced in the carbonisation of coal, except that it may contain not more than 25 per cent. of pitch derived from tar produced in the manufacture of carburetted water gas.

Fractionation

5. On distillation in a litre fractionating flask (a distillation flask without special fractionating column) one-half to two-thirds filled, the pitch shall yield the proportions by weight of distillates stated below ; the temperatures of distillation being read on a thermometer of which the bulb is opposite the side tube of the flask :—

Below 270° C. or 518° F., not more than 1 per cent. of distillate.

Between 270° and 315° C. or 518° and 599° F., not less than 2 per cent. and not more than 5 per cent. of distillate.

" Free Carbon "

6. The pitch shall contain not less than 18 per cent. and not more than 31 per cent. by weight of " free carbon." The " free carbon " is to be determined by the weight of the residue after complete extraction of all matter soluble in benzole or disulphide of carbon. The extraction is best carried out in a Soxhlet or similar apparatus by disulphide of carbon followed by benzole.

TAR OIL

Source of Tar Oil

7. Tar oil to be used is preferably a filtered green or anthracene oil, and shall be derived wholly from tar produced in the carbonisation of coal or from such tar mixed with not more than 25 per cent. of its volume of tar produced in the manufacture of carburetted water gas.

Specific Gravity

8. The specific gravity of the tar oil at 20° C. (68° F.) shall lie between 1·065 and 1·085.

Freedom from Naphthalene and Anthracene

9. The tar oil after standing for half an hour at 20° C. (68° F.) shall remain clear and free from solid matter (naphthalene, anthracene, etc.).

Fractionation

10. The tar oil shall be commercially free from light oils and water. On distillation in a litre fractionating flask (a distillation flask without special fractionating column) one-half to two-thirds filled, the tar oil shall yield the proportions by weight of distillates stated below; the temperatures of distillation being read on a thermometer of which the bulb is opposite the side tube of the flask :—

Below 170° C. or 338° F., not more than 1 per cent. of distillate (light oils and water, if any).

Below 270° C. or 518° F., not more than 30 per cent. of distillate (middle oils, and light oils and water, if any).

Below 330° C. or 626° F., not less than 95 per cent. of distillate (heavy oils, middle oils, and light oils and water, if any).

CREOSOTE OIL

Much has been written on the testing of coal-tar creosote, but up to the present it seems that none of the methods published have been accepted as standard ones. The usual tests to which creosote is submitted are: Determination of specific gravity; and the estimating of the percentage of water, phenols, and naphthalene, and also a distillation test in order to determine the distilling range. Occasionally the percentage of "free carbon" and pyridine bases are estimated. Other tests which are sometimes applied are the solubility of the sample in benzole, the solubility in dimethyl sulphate, flash-point, and coefficient of expansion.

Specific Gravity.—This is determined in a fairly accurate way by the use of a hydrometer, making a correction for temperature, or, better still, cooling a sample down to a prearranged temperature. It is not always possible to take the gravity of a creosote at 15·5° C., as sometimes at this temperature the material is solid or semi-solid. When the oil is liquid at 15·5° C., then it is as well that the gravity be taken at that temperature, but should the oil be solid, then it is necessary, of course, to estimate the gravity at a higher one. Sage recommends taking the specific gravity of salty creosotes at a uniform temperature of 60° C. Butterfield suggests that the gravity of salty creosotes should be determined at the temperature at which the oil is fully liquid. Often specifications state at what temperature the gravity should be taken, but seldom do they mention the method by which the determination is to be made. If it is desired to obtain a more accurate test, then the picnometer or Regnault gravity bottle should be used. Some chemists recommend the employment of a Westphal balance.

Percentage of Water.—This is determined by distilling a measured quantity of the creosote in a retort until no more water is given off. The quantity of oil taken is generally 100 c.c., and the beak of the retort into which it is placed should be long and preferably surrounded by a piece of wet blotting-paper, arranged so that it is possible occasionally to remoisten it during the distilling operation. In any case care must be taken that the distillation is not conducted too rapidly, or else some of the water will not be condensed and will escape as steam. Oil, of course, distils over with the water and sometimes does not separate well in the graduated cylinder in which it is collected. In order, therefore, to bring about a clean separation it is advisable to introduce into the cylinder about 10 c.c. of 90's benzole or solvent naphtha. This will hold in solution any naphthalene which may distil over, should the creosote be a very salty one, and in all cases will result in a clear reading being obtained. It is possible, of course, to estimate the percentage of water in a creosote at the same time as the test is being made for distilling range, and reference will be made to this when dealing with the fractionation of a creosote.

Phenols.—There are several methods of estimating phenolic bodies in creosote. In many laboratories it is determined by taking a measured quantity, generally 100 c.c. of the creosote, and placing it in a separating funnel, and then washing it with two or three successive quantities of caustic soda solution of about 40° Tw. The volumes of soda used are approximately 20 or 25 c.c. for each operation. The soda washings are mixed and acidified with dilute sulphuric acid (1 : 3) and the phenols which are thrown up separated and measured. Of course, should the oil be very salty, it is necessary to heat it to a temperature at which it will remain liquid and also to heat the soda a little before adding it. In cases of this kind the temperature at which the oil is measured should be noted and the tar acids separated should be measured at the same temperature. On the other hand, the creosote may be weighed and the tar acids which are separated weighed also. Should the creosote be liquid at normal temperature, then a rough method for determining the tar acids is the following : 50 c.c. of 40 Tw. caustic soda are placed in a 100 c.c. graduated and stoppered test mixer. On the top of this are run 50 c.c. of the creosote, both materials, of course, being put into the cylinder at the same temperature. The contents of the mixer are agitated and then allowed to stand to separate. The increase in volume of the soda or the decrease in volume of the creosote will give, when multiplied by two, the percentage of tar acids.

Another method of estimating the phenols is to distil 100 c.c. of the creosote in a retort and collect all that will come over up to 315° C. The distillate is heated if necessary and agitated in a separating funnel with three successive quantities of 25 c.c. each of caustic soda solution of a strength of 40° Tw. These soda extracts are carefully separated and mixed together, placed in a clean separating funnel and shaken out with a small quantity of ether in order to remove any entangled hydrocarbon bodies. This extracted soda solution is carefully separated from the ether and heated on the water-bath in order to drive off any ether which has remained in solution. It is then cooled and rendered just acid with dilute sulphuric acid, made by mixing one part of the acid with three of water. The acidification is conveniently conducted in a separating funnel, and after allowing a period of rest for separation, the greater part of the acid sodium sulphate solution may be run off and the remainder, together with the phenols, run into a graduated cylinder, and the volume of the phenols read off. These phenols will, of course, contain a certain amount of dissolved water.

Church recommends distilling 100 c.c. of the creosote, measured at limpid point, in a Jena Wurtz flask. The flask is connected to an air condenser tube, which is kept warm by a Bunsen flame during the operation, to prevent the distillate from solidifying. The operation is continued until 95 per cent. of the creosote has been collected into a specially graduated separating funnel. The contents of the separating funnel are warmed to 60° C. in water and the volume read off. Fifty c.c. of a 10 per cent. solution of caustic soda are now added, and the mixture shaken well and allowed to settle. The clear soda solution is carefully removed, the oil warmed again to 60° C. and the shrinkage noted. Another 30 c.c. of caustic soda solution are added, shaken, separated, etc., and any further shrinkage noted. This operation is repeated until no further shrinkage takes place, and the total shrinkage of the oil is taken as the percentage of tar acids present in the original sample.

Naphthalene.—There are several methods of estimating this material in creosote, and it is very difficult to say which of these methods gives the most accurate results. A rough method of estimating this material is the following: 25 grams of the creosote are weighed in a beaker to the second decimal place, and kept at a temperature of between 50° and 60° F. for twelve hours, then at 60° F. for two hours, with constant stirring. The contents of the beaker are then carefully but rapidly transferred to a larger filter paper supported in a funnel, which in its turn is supported in a water jacket, the water of which is kept at a temperature of 60° F. Draining is allowed to take place until the mass becomes fairly solid on the filter paper, when the filter paper and the contents are removed from the funnel, the top of the paper folded over and the lot placed between folds of blotting-paper and pressed under a copying press. The latter portion of this operation must be conducted very rapidly, in order to avoid any serious rise in temperature. After the pressing, the naphthalene is very carefully scraped off the filter paper into a tared dish and weighed. Sometimes the creosote is cooled to 32° F. (0° C.) for four, twelve, or twenty-four hours before separating the naphthalene as just described.

Sage recommends that the naphthalene should be estimated in the fractions of creosote distilling below 270° C., and not in the entire oil, by filtering the cooled distillate through filter cloth and pressing between bibulous paper. Mann estimates naphthalene by determining the "latent heat point" in a special apparatus. The method is fully described in the original paper by this worker.[1]

The apparatus used in Mann's method is illustrated in Fig. 129 and the test is made as follows: A portion of the sample, about 50 c.c., is distilled from a small retort until incipient decomposition of the residue is observed, and the collected distillate is warmed until wholly fluid and then well mixed. The small tube A is removed from the apparatus and filled about two-thirds with the distillate. This is gradually cooled, stirring all the time with a thermometer calibrated in 0·2° C., until it becomes opaque, owing to the formation of crystals, and the temperature at which the opaqueness appears is noted. The water in the water-jacket C and the air-bath B (see Fig. 129) are then brought to a temperature two or three degrees lower than the opacity point temperature just obtained. The distillate in A is then remelted and again cooled carefully to opacity point, when the tube is placed into B. Then the thermometer in A is adjusted so that it is quite central and the bottom of its bulb about 2 cm. from the bottom of the tube. The temperature will be noticed to rise slightly and then remain constant for about half a minute, after which it commences to fall. The maximum temperature reached is taken as the "latent heat point." In the original paper a curve is shown, the ordinates of which give the "latent heat point" in degrees centigrade and the abscissæ percentage of naphthalene. From this curve and the latent heat point obtained, the percentage of naphthalene in any sample may be found. It is advisable for each worker to plot his own curve in the first instance, but the following figures may be useful to those who do not wish to carry out the experimental work necessary to construct a curve:—

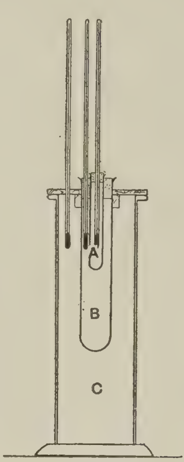

FIG. 129.—APPARATUS USED IN MANN'S METHOD OF ESTIMATING NAPHTHALENE IN CREOSOTE.

Actual percentage of Naphthalene.	"Latent Heat Point."
20	30° C.
25	34° C.
30	40° C.
35	45·5° C.
40	49·8° C.
45	52° C.

Church recommends the following method: The extracted oil from the tar acid estimation (see page 392, Church's method) is placed in a copper beaker and kept at a temperature of 15·5° C. for fifteen minutes. The mass is then filtered on a perforated funnel connected to a suction pump and sucked dry, and the naphthalene in the filter then pressed between blotting-paper in a letterpress to remove all oil, and weighed. The percentage of this material is figured on the weights of original oil, as given by the specific gravity at the limpid point. Church estimates the limpid point by taking 5 c.c. of the creosote in a test tube at 60° C. cooling, and stirring with a thermometer until the first crystals begin to form (limpid point). Cooling in water should be carried out if necessary.

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[1] "Notes on the Testing of Coal Tar Creosote," J. C. Mann. *J.S.C.I.*, June 30th, 1910, p. 732.

According to J. M. Weiss[1] naphthalene or "dry salts" may be determined in tar oils as follows :—

The tar acids are first of all extracted by shaking out with sodium hydroxide solution, the oil allowed to drain and then cooled to 4·5° C. The separated solids are collected, dried between filter paper, and weighed. In connection with the subject of naphthalene, this author determines what is called the "limpid" point of the oil by cooling it until crystals appear, and then raising the temperature until all the crystals disappear, the point at which this happens constituting the limpid point.

R. Mezger[2] gives the following method for the estimation of naphthalene in tar oils. An accurate quantity of tar oil, say, 0·4 to 1 gram, is weighed into a flask and 5 c.c. of 15 per cent. phosphoric acid added. A current of purified coal gas is passed through the contents of this flask, and as it issues it is led into a potash bulb half-full of concentrated potassium hydroxide solution (1 part of water, 1 part of potassium hydrate). During the estimation, the potash bulb and the flask are suspended in a vessel of water, the temperature of which is kept at about 70° C. The rate at which the gas is passed through the apparatus is about 25 litres per hour, and the process is continued for 3½ hours. The gas on leaving the potash bulb is passed through a scrubber which consists of a reservoir and a bulb tube, the latter sloping upwards from the former. This scrubber contains 50 c.c. of saturated picric acid solution. After the expiration of the 3½ hours the contents of the scrubber are placed on a filter, the scrubber washed out with water and the washings also passed through the filter. The filter is then thoroughly washed with water, and the filtrate is titrated with N/10 sodium hydroxide solution, using as indicator sodium alizarinsulphonate.

Distilling Range.—A very usual practice for obtaining the distilling range of a creosote in this country is to distil 100 c.c. of the oil in an 8-ounce tubulated retort, no condenser being connected to the same. The position of the thermometer varies according to individual ideas or the requirements of specifications. Some recent workers have adopted the use of a Wurtz distilling flask connected to an air-cooled condenser. In the author's opinion the Wurtz flask method is certainly the best. The tarworks chemist will find that specifications require the use of either a retort or flask, the size of which may vary. The position of the bulb of the thermometer is sometimes not stated ; at others, in the case of a retort, it is required to be in the liquid at the commencement of the distillation, or else above the liquid, and in the case of a distilling flask, just above the surface of the liquid at the commencement of the distillation, immediately opposite the outlet tube, just below the outlet tube, and just above the outlet tube. The rate of distillation is sometimes mentioned and at others it is not. As a matter of fact there is at the present moment a great need for the adoption of a standard method of obtaining the distilling range of a creosote.[1]

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[1] *Jour. Ind. Eng. Chem.*, 1918, 10, 911–916.

[2] *Gas und Wasserfach*, 1921, 64, 413–416. A further paper on this subject by Knublauch will be found in *J. Gasbeleucht*, 1918, 61, 134–137 and 145–149, which is abstracted in the *J.S.C.I.*, August 31st, 1918, p. 458A.

The following details will illustrate this point: A virgin heavy creosote collected from coal tar between the cut points of 4° Tw. and 15½° Tw. was submitted to distillation in a retort, and also in two different sizes of Wurtz flasks. The oil had a specific gravity of 1·057 @ 15° C. and 1·054 @ 20° C., and was free from naphthalene salts @ 15° C. The retort was of the usual 8 ounce size, tubulated. The beak was 14½ inches long, ½ inch internal diameter at the exit, and 1½ inches internal at the entry, and the bulb was 4½ inches from bottom to top. Wurtz flask A was a 100 c.c. flask; the over-all dimensions being 7½ inches, and the bulb 2¾ inches in diameter. The outlet tube was ¾ inch above the top of the bulb, and was connected to a glass tube of 1 inch internal diameter. The total length of the outlet-tube and glass tube condenser when fitted up was 14½ inches. Wurtz flask B was a 200 c.c. flask, over-all dimensions 10½ inches, distance of the outlet-tube from top of the bulb 3½ inches, diameter of the bulb 3½ inches. When the outlet-tube was connected to a 1-inch (internal) tube, to act as a condenser, the total length was 14½ inches. In both cases the thermometer bulb was placed just opposite the outlet tube; and in flask A the bottom of the bulb was 1¼ inches above the liquid at the commencement of the distillation, while in flask B it was 4¾ inches. The table below gives the figures obtained.

—	Retort.				
	Ther. in liquid bulb ⅜-inch from bottom of retort.	Ther. in liquid bulb ⅜-inch from bottom of retort. Retort bulb covered with a sheet of asbestos bent round.	Ther. in liquid bulb ⅜-inch from bottom of retort. Retort bulb covered with tin hood packed with asbestos.	Wurtz flask A.	Wurtz flask B.
Below 140° C. .	0·85	0·25	0·25	0·8	1·1
140°–270° C. .	41·00	40·00	45·00	58·0	56·0
270°–300° C. .	21·00	23·00	22·00	15·0	14·0
Total Distillate .	62·85	63·25	67·25	73·8	71·1

Sage recommends the use of an 8-oz. retort, the upper part of the bulb of which is covered with a tin can packed with asbestos. With reference to the position of the bulb of the thermometer, this he recommends to be in the liquid at the commencement of the distillation and not more than ½ inch from the bottom of the retort. With reference to the points at which fractions should be collected, he gives the following:

(*a*) Distillate up to 210° C.
(*b*) ,, between 210 to 235° C.
(*c*) ,, ,, 235 to 270° C.
(*d*) ,, ,, 270 to 315° C.
(*e*) Residue not distilling at 315° C.

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[1] "Investigations on Coal Tar and some of its Products," A. R. Warnes and W. B. Southerton, *Trans. of the Midland Junior Gas Association*, 1911–1912.

With reference to these points it should be borne in mind that usually specifications detail the points at which the fractions must be taken.

Church favours the method given in the *American Railway Engineering and Maintenance of Way Association Bulletin*, No. 65. In this method a retort is used connected to an air-cooled condenser, the maximum distance from the centre of the bulb of the retort and the end of the condenser being 24 inches. The thermometer, which is a standard one, is inserted in the retort in such a fashion that the lower end of the bulb is ½ inch from the surface of the oil at the commencement of the distillation. The retort is covered with an asbestos paper cover and supported on a piece of wire gauze. It is heated with a Bunsen burner surrounded by a chimney. The distillates are collected in weighed bottles, and all the fractions determined by weight, this necessitating, of course, the weighing into the retort of 100 grams of the oil. When any measurable quantity of water is present in the oil, the distillation should be stopped at the point it ceases to come over ; the oil is then separated from the water and returned to the retort, when the distillation should be recommenced.

Reports are made on the following fractions :

0 to 170° C.
170 ,, 200° C.
200 ,, 210° C.
210 ,, 235° C.
235 ,, 270° C.
270 ,, 315° C.
315 ,, 335° C.

Estimation of " Free Carbon."—This comes under the head of insolubility in benzole and is determined at the same time as a solubility in benzole test. Sage recommends the following method for creosote containing no water. One hundred grams of the creosote should be filtered whilst hot through a tared filter paper, and the filter paper afterwards washed with benzole in a Soxhlet extraction tube until the benzole runs away clear. The filter is then dried and weighed. He considers that in no case should more than 0·25 per cent. of insoluble matter be passed without comment. Should the creosote contain more than a trace of water this may be driven off first in the usual fashion, separated from the oil which comes over, the oil added to the material in the retort, and the whole lot, while warm, passed through a tared filter paper as just described.

Pyridine Bases.—These may be estimated in the creosote by shaking out, say, 100 c.c. in a separating funnel with dilute sulphuric acid (1 : 2), using three lots of about 25 c.c. each. The acid extractions are bulked, washed with a little ether, separated, the ether which remains in solution in the acid extract driven off on the water-bath, and the pyridine bases then thrown up by adding to the acid extract caustic soda of about 40° Tw. strength. The bases are separated and dried by treatment with 90° Tw. caustic soda and then their volume read off. Occasionally the bases are not extracted from the oil as received, but 100 c.c. are distilled in the retort up to 315° C. and the bases determined in the distillate.

The Dimethyl Sulphate Test.—Dimethyl sulphate will not dissolve, to any appreciable extent, paraffin or olefine hydrocarbons, but dissolves benzene and its homologues. On account of this fact, this compound has been used to determine approximately the amount of mineral oil or paraffinoid bodies in creosote. Dr. Sommer recommends the following method: Four c.c. of the distillate are put in a 10 c.c. graduated cylinder provided with a stopper and 6 c.c. of dimethyl sulphate added, after which the contents are shaken thoroughly for one minute. If the distillate is not entirely soluble, a separation will take place within a few minutes, and the line of separation, being clear, can be easily read.

Flash Point.—As creosote flashes at a fairly high temperature, it is not possible to use the Abel test apparatus and obtain satisfactory results. The best apparatus to use for determining the flash point of creosote is that known as the Pensky-Marten. This apparatus consists of an oil cup with cover, to which is fitted a stirrer and thermometer. The bath is heated by a spirit lamp or Bunsen burner, and the slow and regular heating of the oil is ensured by the jacket of air which surrounds the cup.

Sometimes it is necessary to obtain the open flash of creosote. This is determined by taking about 100 c.c. in a porcelain basin and heating it carefully with a Rose burner, stirring all the while with a thermometer. The rate of heating should be about one degree per minute, and at every degree a lighted taper should be passed near the surface of the oil. The temperature is read off immediately a flash is noticed.

Coefficient of Expansion.—The method of determining this constant is not in any way difficult. Sage recommends the following: One hundred c.c. of the creosote should be measured into a flask marked at 100 c.c. on the neck and graduated in one-tenths of a c.c. up to 106 c.c. The volume should be first adjusted to 100 c.c. at 40° C., and the flask then warmed in a water-bath to 80° C., and the volume at that temperature measured and recorded. The factor most commonly employed is an expansion of 1 per cent. for a rise of every 22½° F., but this is not true for all creosotes or for high temperatures as well as low ones. Sage has plotted curves obtained when heating samples from 20° C. to 80° C., and the range falls within very narrow limits, his results showing that the increase in volume is 1 per cent. for each 13·3° C., or approximately 1 per cent. for every 24° F.

BRITISH STANDARD SPECIFICATION FOR CREOSOTE

The following tests are reprinted by permission of the British Engineering Standards Association from B.S. Specification No. 144, for creosote for the preservation of timber.[1]

This Specification covers the requirements of Creosote suitable for the treatment of Railway Sleepers and Telegraph, Telephone, and Hangar Poles.

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[1] Official copies of this Specification can be obtained from the Secretary of the Association, 28 Victoria Street, London. Price 1*s.* 2*d.* net, post free.

Type A

Description

1. The material shall consist essentially of a distillate of coal tar, and shall be free from any admixture of petroleum or similar oils.

Specific Gravity

2. (See Appendix I.) The specific gravity shall be not less than 1·015 and not more than 1·07 at 38° C. (100° F.) when compared with water at the same temperature.

Fluidity

3. The material shall become completely liquid on being slowly warmed to 38° C. (100° F.) with stirring, and on cooling down shall remain completely liquid after standing for two hours at 32° C. (90° F.).

Water Content

4. The amount of water in the creosote shall not exceed 3 per cent. when determined by the method described in Appendix II.

Distillation

5. When 100 c.c. measured at 38° C. (100° F.) of the dry creosote are distilled from a 250 c.c. distillation flask (see Appendix III) at such a rate that the distillation is complete in about 20 minutes, there shall distil at 760 mm. pressure,

Up to 205° C. (401° F.) not more than 7 c.c.
,, 230° C. (446° F.) ,, ,, 40 ,,
,, 315° C. (599° F.) ,, ,, 78 ,,

the volumes of all fractions being measured at 38° C. (100° F.).

The residue above 315° C. (599° F.) shall be soft and not sticky, and its weight shall be not less than 22 grams.

Tar Acids

6. The amount of Tar Acids when determined by the method described in Appendix IV shall be not less than 5 per cent. and not more than 16 per cent. by volume.

Matter Insoluble in Benzole (Benzene)

7. The amount of matter insoluble in benzole (benzene) shall not exceed 0·4 per cent. by weight.

ADDENDUM

Type B

Alternative for Scotch Creosote

Scotch creosote shall conform to the above specification with the following exceptions :—

2. *Specific Gravity.*—The specific gravity shall be not less than 1 at 38° C. (100° F.). In the case of the blast-furnace oil the specific gravity may be lower, but shall not be less than 0·940 at 38° C. (100° F.).

5. *Distillation.*—The distillate at 315° C. (599° F.) shall be not more than 85 c.c. and the residue not less than 15 grams.

6. *Tar Acids.*—There shall be no upper limit to the amount of tar acids.

APPENDIX I

Specific Gravity

Care shall be taken to ensure that the creosote is completely liquefied and homogeneous before the sample is taken.

In the event of the temperature at which the determination is made not being exactly 38° C. (100° F.) the observed specific gravity (d) at the temperature $t°$ shall be converted to "corrected" specific gravity D by means of the formula :—

$$D = d + 0{\cdot}00075\ (t - 38)$$

if t be in degrees C., or

$$D = d + 0{\cdot}00042\ (t - 100)$$

if t be in degrees F.

APPENDIX II

Determination of Water Content

The material shall be made completely liquid and homogeneous by warming to 38° C. (100° F.). One hundred c.c. of the liquid measured at 38° C. (100° F.) shall be mixed with 50 c.c. of xylol previously saturated with water, and the mixture distilled from a distillation flask, at the rate of about 3 c.c. per minute. Fifty c.c. of distillate shall be collected in a cylinder of suitable size, graduated in 1/5 c.c., and the volume of water determined at room temperature.

The condenser used in this test shall be either a straight vertical condenser, or of such construction that it will readily drain completely.

APPENDIX III

Distillation

The creosote shall be dried over calcium chloride, plaster of Paris, or other suitable material, and 100 c.c. of the dried creosote measured at 38° C. (100° F.) placed in a tared standard 250 c.c. Wurtz distillation flask, the neck of which is approximately 12 cm. long with outlet tube emerging approximately half-way up the neck. The flask shall be furnished with a standardised thermometer, the top of the bulb of which is just below the outlet tube. The distillation shall be carried out over a free flame. When a temperature of 315° C. (599° F.) has been reached, the distillation shall be stopped, the flask and contents allowed to cool and then reweighed.

Correction for Emergent Thread of the Thermometer

The number of degrees C. (dt) to be added to the observed thermometer reading t° C. shall be calculated from the following formula :—

$dt = 0{\cdot}000143\ (t - t')N$, where N is the number of degree divisions of thread exposed above the cork and t' the air temperature half-way up the exposed thread.

When Fahrenheit thermometers are used, the formula shall be,

$$dt = 0{\cdot}0000794\ (t - t')N.$$

Correction for Barometric Pressure

For every 25 mm. above or below 760 mm., 0·8 gram (0·6 gram in the case of Scotch oils) shall be subtracted from or added to the observed weight of residue in the flask.

APPENDIX IV

Determination of the Tar Acids

The tar acids shall be determined by complete extraction of the total distillate below 315° C. (599° F.) with caustic soda solution of specific gravity 1·18. The tar acids shall be separated from the soda solution by neutralising with sulphuric acid (specific gravity 1·35 at 15° C. (59° F.) *i.e.*, one volume of 1·84 acid mixed with two volumes of water) and their volume determined.

The following tests for creosote oil for using in the preservation of ties and structural timber are inserted by the permission of The American Wood Preservers' Association, to whom the author makes his acknowledgments.

Creosote Oil for Ties and Structural Timber [1]

The oil shall be a distillate of coal-gas tar or coke-oven tar. It shall comply with the following requirements :—

1. It shall not contain more than 3 per cent. of water.
2. It shall not contain more than 0·5 per cent. of matter insoluble in benzole.
3. The specific gravity of the oil at 38° compared with water at 15·5° C. shall be not less than 1·03.
4. The distillate, based on water-free oil, shall be within the following limits :

Up to 210° C. not more than 5 per cent.
Up to 235° C. not more than 25 per cent.

5. The specific gravity of the fraction between 235° C. and 315° C. shall be not less than 1·03 at 38° compared with water at 15·5° C.

The specific gravity of the fraction between 315° and 355° C. shall be not less than 1·10 at 38° compared with water at 15·5° C.

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[1] Report of Proceedings, 13th Annual Meeting, *A.W.P.A.*, 1917, p. 307.

6. The residue above 355°, if it exceeds 5 per cent., shall have a float-test of not more than 50 seconds at 70° C.

7. The oil shall yield not more than 2 per cent. coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

Creosote Oil, Grade 2, for Ties and Structural Timber [1]

The oil shall be a distillate of coal-gas tar or coke-oven tar. It shall comply with the following requirements :—

1. It shall not contain more than 3 per cent. of water.
2. It shall not contain more than 0·5 per cent. of matter insoluble in benzole.
3. The specific gravity of the oil at 38° compared with water at 15·5° C. shall be not less than 1·03.
4. The distillate, based on water-free oil, shall be within the following limits :

Up to 210° C. not more than 8 per cent.
Up to 235° C. not more than 35 per cent.

5. The specific gravity of the fraction between 235° and 315° C. shall be not less than 1·03 at 38° compared with water at 15·5° C.

The specific gravity of the fraction between 315° and 355° C. shall be not less than 1·10 at 38° compared with water at 15·5° C.

6. The residue above 355°, if it exceeds 5 per cent., shall have a float test of not more than 50 seconds at 70° C.

7. The oil shall yield not more than 2 per cent. coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

Creosote Oil, Grade 3, for Ties and Structural Timber [2]

The oil shall be a distillate of coal-gas tar or coke-oven tar. It shall comply with the following requirements :—

1. It shall not contain more than 3 per cent. of water.
2. It shall not contain more than 0·5 per cent. of matter insoluble in benzole.
3. The specific gravity of the oil at 38° compared with water at 15·5° C. shall be not less than 1·03.
4. The distillate, based on water-free oil, shall be within the following limits :

Up to 210° C, not more than 10 per cent.
Up to 235° C, not more than 40 per cent.

5. The specific gravity of the fraction between 235° and 315° C. shall be not less than 1·03 at 38° compared with water at 15·5° C.

The specific gravity of the fraction between 315° C. and 355° C. shall be not less than 1·10 at 38° compared with water at 15·5° C.

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[1] Report of Proceedings, 14th Annual Meeting, *A.W.P.A.*, 1918, p. 172.

[2] *Ibid.*

6. The residue above 355° C., if it exceeds 5 per cent., shall have a float test of not more than 50 seconds at 70° C.

7. The oil shall yield not more than 2 per cent. coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

Distillate Oil for Non-pressure Treatments [1]

The oil shall be a distillate of coal-gas tar or coke-oven tar. It shall comply with the following requirements :—

1. It shall be thoroughly liquid at 15° C.
2. It shall not contain more than 0·5 per cent. of matter insoluble in benzole.
3. The specific gravity of the oil at 38°/15·5° C. shall be not less than 1·06.
4. The distillate, based on water-free oil, shall be within the following limits :

Up to 210° C. not more than 1 per cent.
Up to 235° C. not more than 10 per cent.

5. The specific gravity of the fraction between 235° and 315° C. shall be not less than 1·03 at 38°/15·5° C.

The specific gravity of the fraction between 315° and 355° C. shall be not less than 1·10 at 38°/15·5° C.

6. The residue above 355° C., if it exceeds 10 per cent., shall have a float test of not more than 50 seconds at 70° C.

7. The oil shall yield not more than 2 per cent. coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

Creosote Coal-Tar Solution for Ties and Structural Timber [2]

The oil shall be a coal-tar product, of which at least 80 per cent. shall be a distillate of coal-gas tar or coke-oven tar, and the remainder shall be refined or filtered coal-gas tar or coke-oven tar. It shall comply with the following requirements :—

1. It shall not contain more than 3 per cent. of water.
2. It shall not contain more than 2 per cent. of matter insoluble in benzole.
3. The specific gravity of the oil at 38° compared with water at 15·5° C. shall be not less than 1·05 or more than 1·12.
4. The distillate, based on water-free oil, shall be within the following limits :

Up to 210° C. not more than 5 per cent.
Up to 235° C. not more than 25 per cent.

5. The specific gravity of the fraction between 235° and 315° C. shall be not less than 1·03 at 38° compared with water at 15·5° C.

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[1] Report of Proceedings, 14th Annual Meeting, *A.W.P.A.*, 1918, p. 174.

[2] Report of Proceedings, 13th Annual Meeting, *A.W.P.A.*, 1917, p. 307.

The specific gravity of the fraction between 315° and 355° C. shall be not less than 1·10 at 38° compared with water at 15·5° C.

6. The residue above 355° C., if it exceeds 26 per cent., shall have a float test of not more than 50 seconds at 70° C.

7. The oil shall yield not more than 6 per cent. coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

Coal-Tar Oil for Paving Blocks

The oil shall be a coal-tar product, of which at least 65 per cent. shall be a distillate of coal-gas or coke-oven tar, and the remainder shall be refined or filtered coal-gas tar or coke-oven tar.

It shall comply with the following requirements :—

1. It shall not contain more than 3 per cent. of water.

2. It shall not contain more than 3 per cent. of matter insoluble in benzole.

3. The specific gravity of the oil at 38° compared with water at 15·5° C. shall be not less than 1·07 or more than 1·14.

4. The distillate, based on water-free oil, shall be within the following limits :

Up to 210° C. not more than 5 per cent.
Up to 235° C. not more than 25 per cent.

5. The specific gravity of the fraction between 235° and 315° C. shall be not less than 1·03 at 38° compared with water at 15·5° C.

The specific gravity of the fraction between 315° and 355° C. shall be not less than 1·10 at 38° compared with water at 15·5° C.

6. The residue above 355° C., if it exceeds 35 per cent., shall have a float test of not more than 80 seconds at 70° C.

7. The oil shall yield not more than 10 per cent. coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

Distillate Oil for Paving Blocks

The oil shall be a distillate of coal-gas tar or coke-oven tar. It shall comply with the following requirements :—

1. It shall not contain more than 3 per cent. of water.

2. It shall not contain more than 0·5 per cent. of matter insoluble in benzole.

3. The specific gravity of the oil at 38° compared with water at 15·5° C. shall be not less than 1·06.

4. The distillate, based on water-free oil, shall be within the following limits :

Up to 210° C. not more than 5 per cent.
Up to 235° C. not more than 15 per cent.

5. The specific gravity of the fraction between 235° and 315° C. shall be not less than 1·03 at 38° compared with water at 15·5° C.

The specific gravity of the fraction between 315° and 355° C. shall be not less than 1·10 at 38° compared with water at 15·5° C.

6. The residue above 355° C., if it exceeds 10 per cent., shall have a float test of not more than 50 seconds at 70° C.

7. The oil shall yield not more than 2 per cent. coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

The Committee recommends for adoption the following methods of testing :—

1.—*Water*

Apparatus.—Copper stills, shown in Figs. 130 and 131 below.

Method.—When any measurable amount of water is present in the distillate below 210°, on testing in accordance with Section 4, Distillation, the oil and water in this fraction shall be separated, if possible, and measured separately. If more than 2 per cent. of water is present, or if the water is apparently present to an extent in excess of 2 per cent. but an accurate separation is impossible, the percentage of water present shall be determined by the following method, and the water-free oil so obtained shall be used in distillation test, as described under Section 4.

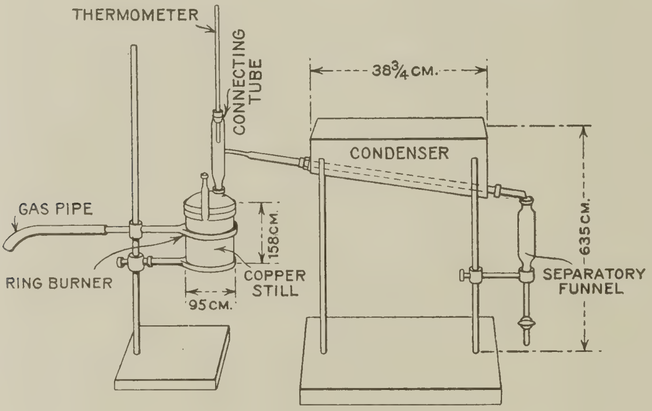

Fig. 130.

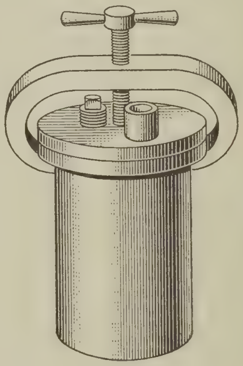

Fig. 131.

Measure 200 c.c. of oil in graduated cylinder, and pour into copper still, allowing the cylinder to drain into the still for several minutes. Attach lid and clamp, using a paper gasket slightly wet with oil around the flange of the still. Apply heat by means of the ring burner, which should be placed just above the level of the oil in the still at the beginning of the test, and gradually lowered when most of the water has distilled over. Continue the distillation until the vapour temperature, indicated by the thermometer with the bulb opposite the offtake of the connecting tube, reaches 205° C. Collect distillate in separatory funnel.

When the distillation is completed, and a clear separation of water and oil in the funnel has taken place, the water is read by volume and drawn off, and whatever light oil has distilled over with the water is then returned to the oil in the still. The dehydrated oil from the still is then taken for distillation, described in Section 4, Distillation.

2.—*Insoluble in Benzole*

Apparatus.—(A) Extractor may be of the form shown in Fig. 132, or any similar form in which the oil is subjected to direct washing by the boiling vapours of the solvent.

(B) Filtering medium may be either two thicknesses of S. and S. No. 575 or Whatman No. 5 hardened filter paper, 15 c.m. in diameter, arranged in cup-shape by folding symmetrically; or alundum thimbles, flat bottom, 30×80 RA 98. If filter papers are used, prior to using they shall be soaked in benzole to remove grease, dried in a steam oven and kept in a desiccator until ready to be used. The filter-paper cup may be suspended in the extractor flask by a wire basket hung from two small hooks on the under surface of the metal cover of the flask.

If the alundum thimble is used, it may be supported by making two perforations in the top of the thimble, and suspending from the cover by German silver or platinum wires.

Method.—Weigh 10 grams of dry oil in 100 c.c. beaker. Add about 50 c.c. of pure benzole, and transfer at once to the filter cup. The filter cup or thimble is previously weighed, and the paper cup shall always be kept in a weighing bottle until ready for use. Wash out the beaker with benzole, passing all washings through the filter cup, and place the latter at once in the extraction apparatus.

Extractor shall contain a suitable quantity of pure benzole. Sufficient heat to boil the solvent shall be provided by means of an electric heater or a steam bath.

Continue the extraction until the descending solvent is practically colourless, and remove the filter cup and dry in steam oven until all solvent is driven off; cool in desiccator and weigh. The balance used for this purpose should be accurate to 0·5 m.g.

3.—*Specific Gravity*

Apparatus.—(A) Hydrometer shall be of the form and dimensions shown in Fig. 133. It shall be standardized at 15·5° C. A set of two with ranges 1·00 to 1·08 and 1·07 to 1·15 will suffice.

(B) Cylinder shall be of the form and dimensions shown in Fig. 134.

Method.—The oil shall be brought to a temperature of 38° C. (100° F.), and the determination shall be made at that temperature unless the oil is not entirely liquid at 38° C. In case the oil requires to be brought to a higher temperature than 38° in order to render it completely fluid, it shall be tested at the lowest temperature at which it is completely fluid, and a correction made by adding 0·0008 to the observed specific gravity for each degree Centigrade above 38° C. at which the test is made. This correction factor does not apply with equal accuracy to all oils, but serious error due to its use will be avoided if the foregoing precaution is observed, with respect to avoiding unnecessarily high temperature.

[1] The expression "38°/15·5° C." means specific gravity taken at 38° C. compared with water at 15·5° C. This cannot be determined directly. The specific gravity is first determined at 38° C. compared with water at 38° C., and this determination represents the relation of the weight of a volume of oil at 38° C. to the weight of an equal volume of water at the same temperature. The relation to an equal volume of water at 15·5° C. is obtained by multiplying the former figure by ·99385, the density of water at 38° C. compared to water at 15·5° C.

From the foregoing it will be readily seen that it is incorrect to calculate the specific gravity at 38°/15·5° C. by dividing the weight of oil taken at 38° C. by the weight of water taken at 15·5° C. An example is given herewith of the correct and incorrect methods of calculating; where the weight of a specific gravity bottle is 23·7531; the weight of the bottle filled with water up to the mark at 15·5° C. is 78·3600; the weight of the bottle plus water at 38° C. is 78·1128; the weight of the bottle filled with oil at 38° C. is 80·2755. The correct calculation therefore would be as follows :—

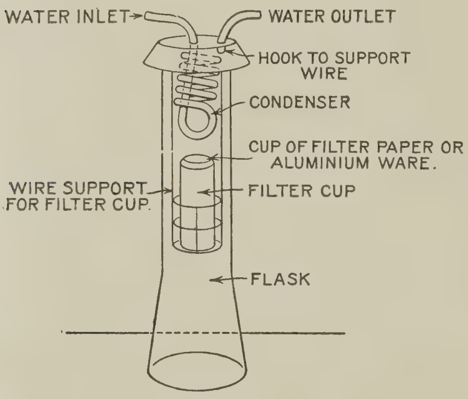

Fig. 132.

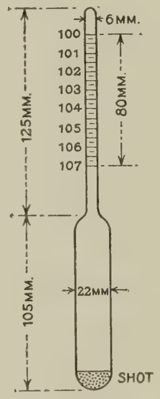

Fig. 133.

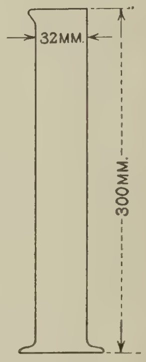

Fig. 134.

Specific gravity at 38/38° C.=

$$\frac{80{\cdot}2755-23{\cdot}7531}{78{\cdot}1128-23{\cdot}7531}=1{\cdot}0398$$

Corrected to 38°/15·5° C.=

$$1{\cdot}0398\times\frac{{\cdot}99299\ \text{(D. water 38°)}}{{\cdot}99913\ \text{(D. water 15°)}}=1{\cdot}0335$$

The incorrect method of calculation is as follows :—

$$\frac{80{\cdot}2755-23{\cdot}7531}{78{\cdot}3600-23{\cdot}7531}=1{\cdot}0351$$

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[1] Report of Proceedings, 14th Annual Meeting, *A.W.P.A.*, 1918, pp. 174–175.

4.—*Distillation* [1]

Apparatus.—(A) Retort shall be a tubulated glass retort of the usual form with a capacity of 250 to 290 c.c. The capacity shall be measured by placing the retort with the bottom of the bulb and the end of the offtake in the same horizontal plane, and pouring water into the bulb through the tubulature until it overflows the offtake. The amount remaining in the bulb shall be considered its capacity (Fig. 135).

(B) Condenser tube of any suitable form of glass tubing may be used; a convenient one is shown in Fig. 136.

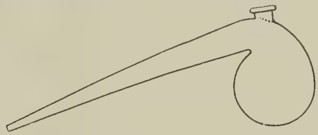

Fig. 135.

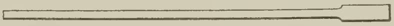

Fig. 136.

(C) Shield of asbestos as shown in Fig. 137 shall be used to protect the retort from air currents, and to prevent radiation. This may be covered with galvanized iron, as such an arrangement is more convenient and more permanent.

(D) Receivers (Erlenmeyer flask) of 50 to 100 c.c. capacity are most convenient form.

(E) Thermometer shall be made of resistance glass of a quality equivalent to suitable grades of Jena or Corning make. It shall be thoroughly annealed. It shall be filled above the mercury with inert gas which will not act chemically on or contaminate the mercury. The pressure of the gas shall be sufficient to prevent separation of the mercury column at all temperatures of the scale. There shall be a reservoir above the final graduation large enough so that the pressure will not become excessive at the highest temperature.

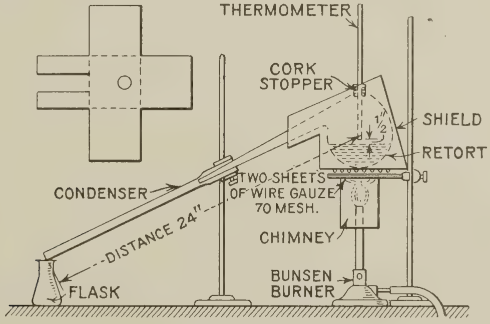

Fig. 137.

The thermometer shall be finished at the top with a small glass ring or button suitable for attaching a tag. Each thermometer shall have for identification the maker's name, a serial number and the letters "A.S.T.M. Distillation."

The thermometer shall be graduated from 0 to 400° C. at intervals of 1° C.

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[1] Report of Proceedings, 13th Annual Meeting, *A.W.P.A.*, 1917, p. 313.

Every fifth graduation shall be longer than the intermediate ones, and every tenth graduation beginning at zero shall be numbered. The graduation marks and numbers shall be clear cut and distinct.

The thermometer shall conform to the following dimensions :—

Total length, mm., 385 maximum.
Diameter of stem, mm., 7, tolerance 0·5.
Diameter of bulb, mm., 5 minimum, and shall not exceed that of the stem.
Length of bulb, mm., 12·5, tolerance 2·5.
Distance 0° to the bottom of bulb, 30, tolerance 5.
Distance 0° to 400° C., 295, tolerance 10.

The accuracy of the thermometer when delivered to the purchaser shall be such that when tested at full immersion the maximum error from 0° to 200° C. shall not exceed 0·5° ; 200° to 300° C. it shall not exceed 1° C. ; 300° to 375° C., it shall not exceed 1·5° C.

The sensitiveness of the thermometer shall be such that when taken at a temperature of 26° C., and plunged into free flow of steam, the meniscus shall pass the 90° C. mark in not more than six seconds.

The retort shall be supported on a tripod or rings over two sheets of 20-mesh gauze, 6 inches square. It shall be connected to the condenser tube by a tight cork joint. The thermometer shall be inserted through a cork in the tubulature with the bottom of the bulb $\frac{1}{2}$ in. from the surface of the oil in the retort. The exact location of the thermometer bulb shall be determined by placing a vertical rule graduated in divisions not exceeding 1/16 in. back of the retort when the latter is in position for the test, and sighting the level of the liquid and the point for the bottom of the thermometer bulb. The distance from the bulb of the thermometer to the outlet end of the condenser tube shall be not more than 24 nor less than 20 ins. The burner shall be protected from draughts by a suitable shield or chimney (Fig. 137).

Method.—Exactly 100 grams of oil shall be weighed into the retorts, the apparatus assembled, and heat applied. The distillation shall be conducted at the rate of at least one drop and not more than two drops per second, and the distillate collected in weighed receivers. The condenser tube shall be warmed whenever necessary to prevent accumulation of solid distillates. Fractions shall be collected at the following points : 210°, 235°, 270°, 315°, and 355° C.

The receivers shall be changed as the mercury passes the dividing temperature for each fraction. When the temperature reaches 355° the flame shall be removed from the retort, and any oil which has condensed in the offtake shall be drained in the 355° fraction.

The residue shall remain in the retort with the cork and the thermometer in position until no vapours are visible ; it shall then be weighed and carefully poured directly into the brass collar for float test (see Section 6), or into a tin box and covered and allowed to cool to air temperature.

If the residue becomes so cool that it cannot be poured readily from the retort, it shall be reheated by holding the bulb of the retort in hot water or steam, and not by the application of flame. The float test shall be made on this residue as described (Section 6).

For weighing the receivers and fractions, a balance accurate to at least 0·05 g. shall be used.

During the progress of the distillation the thermometer shall remain in its original position. No correction shall be made for the emergent stem of the thermometer.

When any measurable amount of water is present in the distillate, it shall be separated as nearly as possible and reported separately, all results being calculated on a basis of dry oil. When more than 2 per cent. of water is present, water-free oil shall be obtained by separately distilling a larger quantity of oil, returning to the oil any oil carried over with the water, and using dried oil for final distillation (See Section 1, Water).

5.—*Specific Gravity of Fractions*

As specific gravity is an absolute physical determination, any recognised method which can be applied to the quantity and quality of material at hand to be tested must be considered satisfactory. The following methods are recommended by the Committee as convenient and accurate means for the relatively small amounts of oil available in determining gravity of fractions to be tested.

Liquid Fractions

Apparatus.—Westphal balance.

Method.—If the fraction to be tested is liquid at a temperature not exceeding 60° C., the Westphal balance can be used with convenience and rapidity. A special type of Westphal balance is obtainable, designed for testing very small quantities. However, the ordinary type Westphal balance can be adapted to testing small fractions by the use of a special plummet. This can readily be made in the laboratory from a piece of ordinary glass tubing 7 mm. outside diameter, sealed at the end, and melting into the glass where sealed a short platinum wire.

After cooling place 9 to 10 grams of mercury in the tube, making a column 35 to 40 mm. high. Seal off the tube within 20 mm. of the top of the mercury column with blowpipe flame. The plummet should have a length of about 55 to 60 mm. over all, and should weigh between 10 and 12 grams.

Solid and Semi-Solid Fractions

Apparatus.—Special platinum or nickel pan as shown in Figs. 138 and 139.

Method.—For the determination of fractions that are solid or semi-solid and cannot readily be liquefied at a temperature not exceeding 60° C., a weighing pan constructed of platinum or nickel (Figs. 138 and 139) may be used.

A pan of convenient dimensions is 20 mm. diameter at the base and 25 mm. diameter at the top, and about 12 mm. deep. It is made of platinum and supported by three platinum wires 1 mm. in diameter, and has a total weight of about 7 grams.

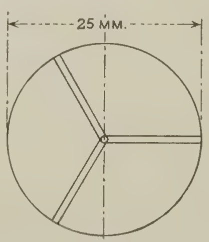

Fig. 138.

Solid or semi-solid fractions of oil can be rapidly and accurately tested in this apparatus by the usual method of weighing in air and in water. The usual precaution, of igniting the pan before use, avoiding the enclosure of air or water in the sample, should be observed.

NOTE.—The method for liquid fractions is usually applicable to the fractions 235 to 315° C. and the method for solid and semi-solid fractions to the fraction 315 to 355° C.

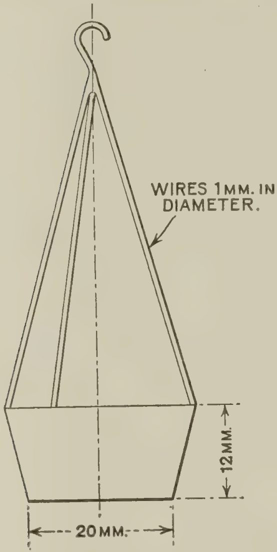

FIG. 139.

6.—*Float Test of Residue*

The residue taken as heretofore described (Section 4) shall be tested for consistency by the float test.

Apparatus.—The float apparatus consists of two parts, an aluminium float or saucer and a conical brass collar (Fig. 140). The two parts are made separately, so that one float may be used with a number of brass collars.

Method.—In making the test, the brass collar is placed with the small end on the brass plate, which has been previously amalgamated with mercury by first rubbing it with a dilute solution of mercuric chloride or nitrate and then with mercury.

The residue to be tested is either poured into the collar direct from the retort, as described in Section 4, or heated in a tin box on water or steam bath, not by direct application of flame, and then poured into the collar in any convenient way, until slightly more than level with the top. The surplus may be removed after the material has cooled to room temperature, by means of spatula or steel knife which has been slightly heated. The collar and plate are then placed in one of the tin cups containing ice water maintained at 5° C., and left in this bath for at least 15 minutes.

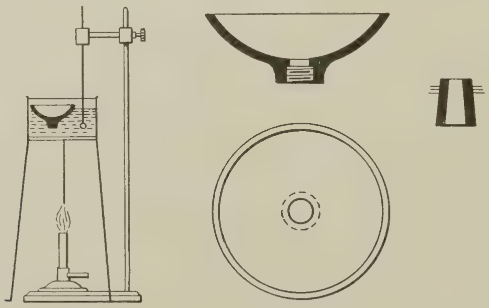

FIG. 140.

Meanwhile the other cup is filled about three-fourths full of water and placed on the tripod, and the water is heated to any desired temperature at which the test is to be made. This temperature should be accurately maintained, and should at no time throughout the entire test be allowed to vary more than one-half a degree Centigrade from the temperature selected.

After the material to be tested has been kept in the ice water for at least 15 minutes and not more than 30 minutes, the collar with its contents is removed from the plate and screwed into the aluminium float, which is then immediately floated in the warmed bath. As the plug of bituminous material becomes warm and fluid, it is forced upward and out of the collar, until the water gains entrance to the saucer and causes it to sink.

The time in seconds between placing the apparatus on the water and when the water breaks through the bitumen is determined by means of a stop-watch, and is taken as a measure of the consistency of the material under examination.

7.—*Coke Residue*

Apparatus.—Hard glass bulbs similar to the one shown in Fig. 141 are to be used.

Method.—Warm the bulb slightly to drive off all moisture, cool in a desiccator, and weigh. Again heat the bulb by placing it momentarily in an open Bunsen flame, and place the tubular underneath the surface of the oil to be tested, and allow the bulb to cool until sufficient oil is sucked in to fill the bulb about two-thirds full.

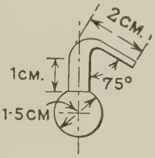

FIG. 141.

Any globules of oil sticking to the inside of the tubular should be drawn into the bulb by shaking or expelled by slightly heating it, and the outer surface should be carefully wiped off and the bulb reweighed. This procedure will give about 1 gram of oil.

Cut a strip of thin asbestos paper about $\frac{1}{4}$ in. wide and about 1 in. long, place it around the neck of the bulb and catch the two free ends close up to the neck with a pair of crucible tongs. The oil should then be distilled off as in making ordinary oil distillation, starting with a very low flame and conducting the distillation as fast as can be maintained without spurting.

When oil ceases to come over, the heat should be increased until the highest temperature of the Bunsen flame is attained, the whole bulb being heated red-hot until evolution of gas ceases, and any carbon sticking to the outside of the tubular is completely burned off. The bulb should then be cooled in a desiccator and weighed and the percentage of coke residue calculated to water-free oil.[1]

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[1] Wide variations in results are obtained when the coke residue of creosote oil is determined by coking in a glass bulb. This is due to the tendency of the glass to fuse at the full temperature required for coking. Very concordant results, slightly lower than the average results with glass bulbs, are obtained by distilling to 355° C. in a retort and coking the residue in a platinum crucible. "Coke Residue Test for Creosote Oils," C. S. Reeve and F. W. Yeager. *Jour. Ind. Eng. Chem.*, 1922, 14, 966–967. See also *J.S.C.I.*, December 15th, 1922, Vol. 41, No. 23, p. 932A.

CALORIFIC VALUE OF FUELS

The importance of an accurate method of determining the heating values of various solid and liquid fuels is now considerable, and for some years the Mahler bomb calorimeter has deservedly been held in high esteem by workers in calorimetry. By means of this apparatus coals, coal tar, creosotes and many other substances are readily examined, and the results arrived at are of an accuracy superior to that obtainable by other and perhaps more frequently employed fuel calorimeters. Recently, the Mahler bomb has been modified by Kroeker,[1] and with this improved apparatus it is possible to correct for the inclusion of the latent heat of the water vapour, which in the furnace of a boiler, for example, escapes, its heat being consequently lost. In Kroeker's bomb there are entrance and exit tubes, by means of which a current of dry air may, after the experiment, be passed through the bomb and the escaping gases and water-vapour collected in the usual weighed calcium chloride tubes and potash bulbs, allowing of a determination of the water and, if desired, of the carbon dioxide produced in the combustion.

In the case of liquid fuels such as tar, creosotes, petroleum fractions, etc., the fuel is placed in a small platinum crucible supplied with the apparatus, and the method then carried out as for solid fuels, the ignition being made by electrical means. The results are accurate, and the apparatus is finding increasing employment at the present time. Figs 142 and 143 show the general appearance of this calorimeter and the bomb in section.

GERMICIDAL VALUE OF COAL-TAR DISINFECTANTS

It has long been recognised that chemical methods of testing disinfectants (especially those of the coal-tar class) are of limited value in appraising their value as germicides, and in 1903 Rideal & Walker introduced their well-known " drop " method, using a standard organism (*B. typhosus*), and comparing the diluted disinfectant with a solution of pure phenol. In spite of much adverse criticism, this method remains the standard procedure for testing disinfectants against a " naked " organism. To perform the test accurately, many precautions have to be taken, and only an expert in its use can obtain trustworthy results.

Briefly, the method consists in shaking together 5 drops (=0·5 c.c., delivered from a special pipette, of a 24-hour-old broth culture grown at 37° C. of *B. typhosus*, or other standard organism selected for the purpose) with 5 c.c. of a known dilution of the disinfectant in sterile distilled water and taking out from the mixture, for subcultivation in broth, a large drop of the liquid every 2½ minutes up to 15 minutes. The subcultures are incubated at 37° C. for 48 hours, when they are examined for signs of growth, and the results carefully noted. A tabulated statement of these results must show a positive result (growth) in the first column (2½ minutes) and a negative result (no growth) in the last (15 minutes). A standard 1 per cent. solution of pure phenol is tested side by side with the disinfectant. Four dilutions of a disinfectant can be tested with the diluted phenol at the same time, a special tube-rack holding these dilutions and thirty tubes of broth (6 sets of 5) being used for convenience of working. The efficiency of the disinfectant is expressed in terms of the standard phenol solution, and when a dilution of the disinfectant has been found which has the same germicidal value in the above test as the standard phenol solution, the former is divided by the latter, when the Rideal & Walker coefficient is obtained. Thus if a 1 in 70 solution of a disinfectant has the same action as a 1 in 80 solution of phenol, the tested disinfectant is not so strong as phenol, and the coefficient is 70/80 or 0·87 (R.W. coefficient).

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[1] The Kroeker modification of the Berthelot-Mahler calorimeter is made in England by Gallenkamp & Co., Ltd., 19 and 21 Sun Street, Finsbury Square, London, E.C., to whom the author is indebted for the loan of the illustration blocks on page 413.

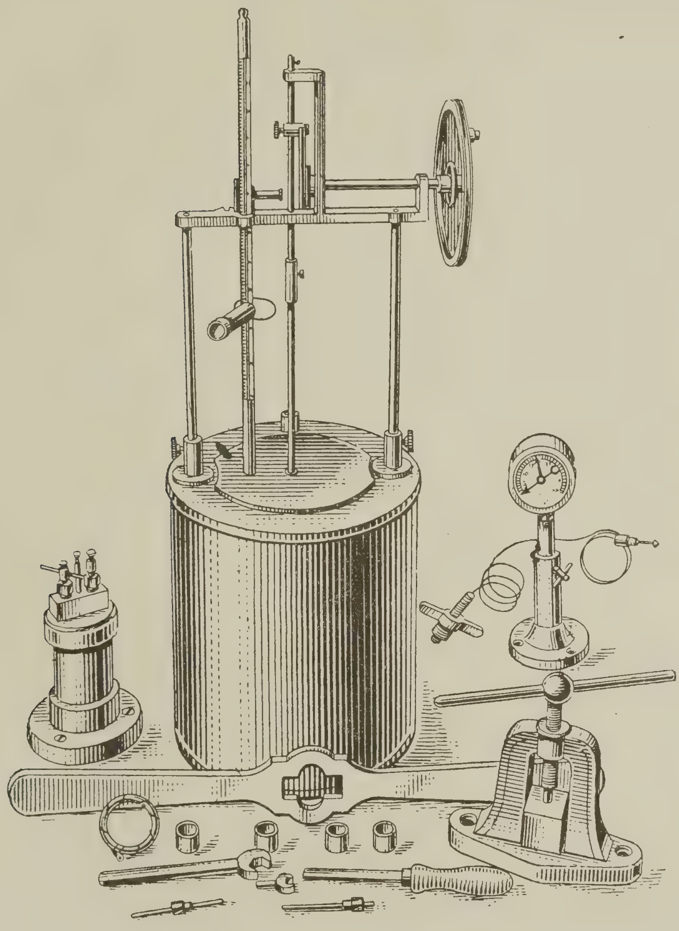

Fig. 142.—Berthelot-Mahler Bomb Calorimeter with Modified Bomb by Dr. K. Kroeker.

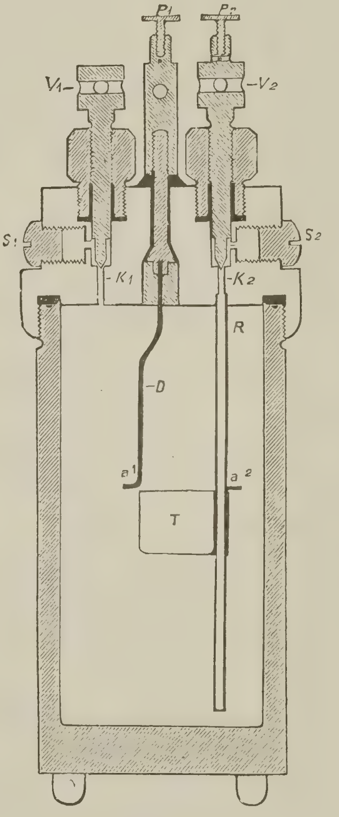

Fig. 143.—Section of Bomb with Kroeker's Modification, showing Platinum Crucible.

A number of precautions must be taken, chief amongst which are: The temperature must not vary more than 2° C. during the carrying out of the tests; pipettes, tubes, and measures, etc., must be sterile; the solidifying point of the standard phenol used for making the test solution must not be below 40° C.—phenol containing cresols is inapplicable; the broth used for cultures should be a "Lemco" broth of prescribed composition, standardised to a +1·5 per cent. reaction (when *B. typhosus* is the test organism).

Further details for carrying out this important test will be found in Moor and Partridge's *Aids to Bacteriology*, third edition, 1916, pp. 258 *et seq.*

It will be seen that in the Rideal-Walker test the culture organism is exposed to the disinfectant in a "naked" condition; that is to say, the conditions of the test do not approximate to the actual circumstances of practical disinfection, where generally the disinfectant comes into contact with pathogenic and other organisms, together with much organic matter of varying nature. For this reason it has been suggested that extraneous organic matter should always be present in the test. It is, however, a matter of some difficulty to prescribe a standard uniform organic addition in suitable amount; and for this reason the Rideal-Walker test in its accepted form should always be carried out without added organic matter, this material being added if desired in another series of tests made separately. The addition of any organic matter tends to lower (sometimes appreciably) the carbolic acid coefficient of the disinfectant.

The following tests will, no doubt, be found very useful to those chemists in tar-works laboratories, who have to deal with road tars and other preparations used in road making. The author has to thank Messrs. Baird and Tatlock, of London, for permission to publish them.

THE FLOAT TEST

Value of this Test

The float test has sometimes been called a viscosity test. This test is always made on viscous and semi-solid refined tars, and often on the viscous and semi-solid petroleum and asphalt products, although when the penetration test can be employed on the two latter classes of material the float test is not always considered necessary. For the more fluid products the test is made at 32° C., and for the semi-solid materials at 50° C. When the material under examination is quite hard, the test may be run at 100° C. The float test is a most convenient one for roughly checking the uniformity of different shipments of bituminous material furnished under specifications. The test fills the gap between the viscosity test and the penetration test, while its chief characteristic is that it is not affected by the presence of mineral matter or "free carbon."

The Test

In making the test the brass collar is placed with the small end down on the brass plate, which has been previously amalgamated with mercury by first rubbing it with a dilute solution of sulphuric or nitric acid, and then with mercury. A small quantity of the material to be tested is heated in the metal spoon until quite fluid, with care that it suffers no appreciable loss by volatilisation, and that it is kept free from air bubbles. It is then poured into the collar in a thin stream until slightly more than level with the top. The surplus may be removed, after the material has cooled to room temperature, by means of a spatula or steel knife which has been slightly heated. The collar and plate are then placed in one of the baths containing ice water maintained at 5° C., and left in this bath for at least 15 minutes. Meanwhile another bath is filled about three-quarters full of water and placed on a tripod, and the water is heated to any desired temperature at which the test is to be made. This temperature should be accurately maintained, and should at no time throughout the test be allowed to vary more than half a degree Centigrade from the temperature selected. After the material to be tested has been cooled in the ice water for about 15 minutes, the collar with its contents is removed from the plate, and screwed into the aluminium float, which is then immediately floated in the warmed bath. As the plug of bituminous material becomes warm and fluid, it is gradually forced upward and out of the collar, until water gains admission into the saucer and causes it to sink.

The time in seconds from the moment the saucer is floated on the water to the moment when water breaks through the bitumen or tar is determined by means of a stop-watch, and is taken as a measure of the consistency of the material under examination.

Fig. 144 illustrates the apparatus required to carry out this test.

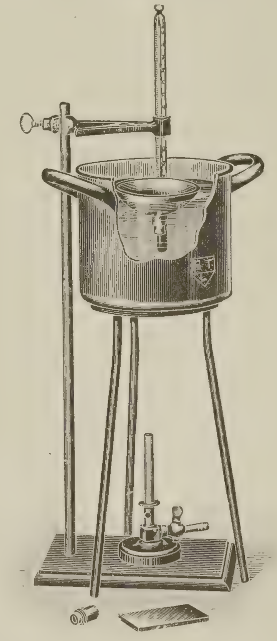
Fig. 144.—Float Test Apparatus.

THE PENETRATION TEST

Value of this Test

This test is made on all semi-solid and solid oil bitumens, asphaltic cements, and native asphalts, and less often on the harder tar products. It is also made on the residues of materials subjected to the volatilisation test, when they are sufficiently hard.

While the standard conditions under which this test is made call for a 100-gram load applied for five seconds on the material maintained at 25° C., it is sometimes desirable, when very soft materials are tested, to make the test with a 50-gram weight. In order to ascertain how susceptible a material may be to temperature changes, tests may be made at any other desired temperatures, preferably at 4° C., with a 200-gram weight for one minute, and at 46° C. with a 50-gram weight for five seconds. In all cases the results of tests should be reported in tenths of a millimetre, and when the term penetration is used without any other qualification, it is understood to refer to the standard test at 25° C., with 100 grams for five seconds. These three temperatures serve as the approximate minimum, average and maximum temperatures to which the paving is likely to be subjected. Asphalt cements produced by the straight distillation of petroleums and those produced by fluxing the native asphalts with straight distilled residual fluxes are more susceptible to temperature changes than those produced by the blowing process. In comparing a straight distilled and a blown asphalt it will be noted that where both may show the same penetration at 25° C., the former will show a lower one at 4° C., and a higher one at 46° C. than the latter. The penetration test, while practically valueless as a means of identification by itself, may be a valuable aid when considered in connection with the specific gravity of the material.

The test is not so useful as a means of control or in the grading of tar residuums used in road construction, because these residuums are quite soft, and as their surface tension is very high they press out or deform under the loaded needle much more than do the asphalt cements commonly used.

The penetration test is one of the most important for examining bituminous materials for determining the adaptability to specific road purposes. It is certainly one of the oldest and most widely used consistency tests.

No very definite limits can be set for the proper penetration of asphalt cements used in road construction, as the limits vary not only with the type of material, but with the conditions it will have to meet under service. The engineer should draw up his specifications in each instance bearing in mind all possible considerations. In general for sheet asphalt and asphaltic concrete the penetration limits will be between 40 and 90, it being customary to allow a five-point margin above and below the penetration selected.

The penetration test is of great importance in the plant inspection of asphalt cements prepared at the paving plant by fluxing refined or native asphalts. Especially when large quantities of asphalt cement are maintained for a long time at elevated temperatures, constant inspection is required, so that if the product hardens, more flux may be added as required. In this connection the engineer should work out his own fluxing curve for a given refined asphalt and a given flux, to determine rapidly the percentage of flux to be added to raise the penetration to any point required.

The Test

The penetration test, see Fig. 145, is made as follows : A sample of the material to be tested is first warmed sufficiently to flow, and poured into the standard copper box. The box and contents, after cooling for half an hour at room temperature, are immersed in water maintained at the temperature at which the test is made (usually 25° C.) and allowed to remain immersed for one and a half hours. The sample in the box should now be placed in the glass cup and removed in it, covered with as much water as convenient without spilling, to the testing shelf on the penetrometer. The rod is lowered until the point of the needle almost touches the surface of the sample ; then it is cautiously pulled down until the needle just comes in contact with the surface of the sample. This can be seen best by having a light so situated that, upon looking through the sides of the glass cup, or through the water above the sample, the needle will be reflected from the surface of the latter. After thus setting the needle the milled button in the centre of the dial is slowly turned until the foot of the rack rests on the head of the rod, and then the dial is brought to zero. The clamp is then opened wide by pressing the button and held in this position for exactly five seconds, as determined by the metronome or watch. The clamp is instantly released, the rack lowered again until it rests on the top of the rod, and the distance travelled by the latter, recorded on the dial as tenths of a millimeter, is the penetration or distance penetrated by the needle.

Owing to the susceptibility of certain bitumens to slight changes in temperature, that of the water bath should be accurately maintained, both before and during the test, and, when the room temperature differs greatly from that of the bath, the water in the glass cup should be renewed after each test. An average of three to five tests, which should not differ more than four points between maximum and minimum, is taken as the penetration of the sample. The tests should be made at points on the surface of the sample not less than one centimetre apart, and not less than one centimetre from the edge of the tin.

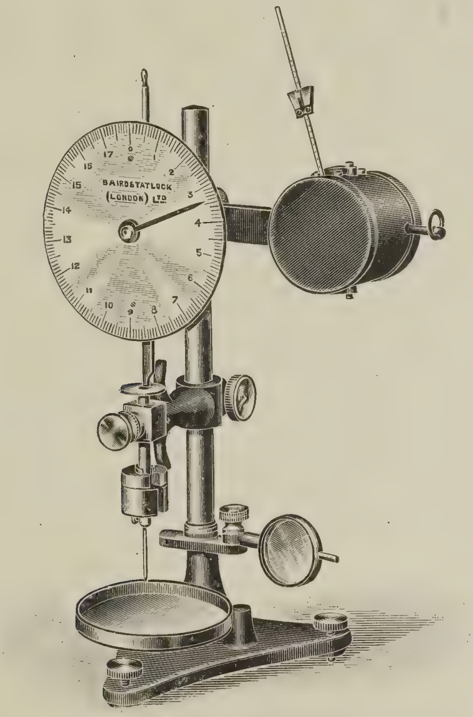

Fig. 145.—B.T.L. Penetrometer; Standard Pattern.

The needle should be removed and thoroughly cleaned by wiping with a dry cloth, after which it is ready for another test. The point of the needle should be examined from time to time with a magnifying glass to see that it is not injured in any way. If it is found defective it must be replaced by a new needle.

DETERMINATION OF MELTING-POINT

Value of this Test

Since bitumens and tars are mixtures of various organic compounds, they can have no true melting-point, but an arbitrary method of determining the so-called melting-point of those materials sufficiently solid to maintain their form for some time under normal conditions is of value as a means of identification and control. The term "fusing-point" is often used in this connection, as the material passes gradually from the solid to the liquid condition, the transition taking place slowly, owing to the heterogeneous character of the substances present. The term "melting-point" is more appropriately applied to chemical substances having a definite composition, which melt sharply and within a narrow temperature range. A number of arbitrary methods for determining the fusing- or melting-point have been tried, but the Ring and Ball method is one of the simplest, most convenient and most commonly used, and has been proposed by the American Society for Testing Materials.

The melting-point determination should be made on all bituminous and tar cements sufficiently hard to be handled at room temperature without distortion in the mould. This test is not usually required for bitumens which are to be cut with a non-volatile flux before use.

The melting-point of a bituminous material is directly related to its hardness and brittleness, but the relations are not the same for all types of materials. A partly blown petroleum residuum may be so manipulated as to obtain a number of combinations of penetration and melting-point. Thus, if a fluid petroleum residuum is blown to a given penetration, its melting-point will be much higher than if the residuum had been reduced to the same penetration by straight distillation. Intermediate melting-points for that penetration may, therefore, be obtained by varying the amount of distillation prior to or with the blowing process. High melting-point materials are as a rule less susceptible to the ordinary temperature changes than those of low melting-point. On the other hand, if the melting-point has been raised by blowing there will be a loss in the ductility of the material at normal or average temperature.

The Test

The material to be tested is first carefully melted in a spoon by the gentle application of heat until sufficiently fluid to pour. When heating care should be taken that no appreciable loss occurs by volatilisation. The two rings which have been placed on an amalgamated brass plate are then filled with the bitumen, and any excess is cut off with a hot spatula when the material has cooled to room temperature. The rings are placed accurately over the round holes on the lower platform of the testing apparatus, and the balls on the centre of the filled rings. The whole apparatus is now stood on the bottom of the glass beaker, filled with about 400 c.c. of water at a temperature of 5° C. Heat is uniformly applied at the bottom of the beaker sufficiently to raise the temperature at the rate of 5° C. per minute. Record the temperature at the start of the test and every minute thereafter until the test is completed. The rate of heating is very important. The softening or melting-point is the temperature at which the sample with the ball has bulged down through the ring and touched the bottom of the beaker, which owing to the special adjustment of the legs of the apparatus is one inch from the platform holding the rings.

Successive tests should average within 3° C. For temperatures above 90° C. glycerine or cotton-seed oil should be used instead of water. The apparatus required for conducting this test is illustrated in Fig. 146.

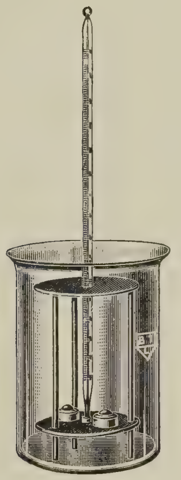

Fig. 146.—Ring and Ball Melting-Point Apparatus.

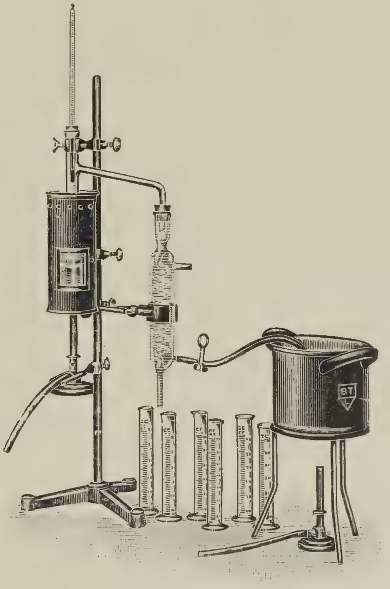

Fig. 147.—Apparatus for Distillation Test of Tars.

DISTILLATION TEST

Value of this Test

The distillation test is made upon tars and tar products, but seldom upon other materials, unless the presence of tar is suspected. The test as applied to tars is valuable both as a means of ascertaining their method of preparation and their suitability for a given purpose. All crude tars contain water, and the appearance of water in the distillate therefore indicates a crude material, especially if accompanied by an appreciable quantity of light oil. Heavy refined tars which have become contaminated with water show a sudden rise in distillation temperature after the water has been removed. The presence of high percentages of naphthalene is indicated by the proportion of the various distillates which solidify upon cooling. In this connection it is always well to note the character of the fractions obtained. The extent of distillation in the manufacture of the original material is indicated by the temperature at which distillation commences in this test, and by the relative quality of each fraction obtained. Cut-back products usually show an abnormal amount of some given fraction as compared to the amount that would be obtained from a straight distilled residue of the same consistency. After the distillation it is often of interest to determine the melting-point of the pitch residue, which, if obtained by distillation to 300° C., should seldom exceed 75° C. The test is thus useful for gauging the uniformity of supply, for factory control, and most of all as a criterion of quality. The distillation test as applied to tars becomes of value in identifying the kind of tar used (upon determining the specific gravity of the fractions distilled), as a means of distinguishing a cut-back tar from a straight-distilled tar (upon determining the specific gravity of the fractions, their viscosity, and the melting-point of the residue), and, as stated above, for determining the presence of abnormal amounts of naphthalene.

The Test

The test briefly consists in distilling 100 c.c. of refined or dehydrated tar in an Engler flask at a uniform rate of 1 c.c. per minute and collecting the various fractions in weighed glass graduates. In preparing for the test it will be found convenient to mark permanently on the foot of each graduate its weight to within one decigram.

The flask should be supported in a vertical position on one pan of a rough balance, and its tare accurately obtained. From the specific gravity of the tar the weight of 100 c.c. is calculated; and this amount, after warming it in a tin cup, if necessary to make it sufficiently fluid, is poured into the flask. It is also expedient to use an Engler flask on which graduation marks of its volumetric contents have been made, and the melted tar may be poured in carefully up to the 100 c.c. mark. A cork stopper carrying the thermometer is then inserted in the neck of the flask, so that the top of the bulb is opposite the middle of the tubulure, and the entire apparatus set up as indicated in Fig. 147. A tin shield with a small hole surrounds the flask and burner, as shown, in order to obviate the influence of draughts. The small hole serves to watch the flame.

The tar should be heated gradually by means of a Bunsen burner, and the heat should be so regulated as to maintain distillation at the constant rate of 1 c.c. per minute. When the thermometer registers a temperature corresponding to 110° C., the graduated cylinder containing the first fraction is replaced by another. The receiver is changed again at 170° C. and at 270° C., using as many graduated cylinders as may be necessary without allowing any one to become filled above the 25 c.c. mark.

When solid matter deposits upon the sides of the condenser, it may be melted by syphoning hot water through the condenser, and collected in the fraction to which it belongs. The last fraction is collected up to 300° C., after which the flask and graduates are cooled to room temperature, and their contents determined by volume and weight. The volume of pitch remaining in the retort is found by deducting the total volume from the original 100 c.c. taken or, if the distillation flask be graduated, a direct approximate reading may be taken. Note should be made of the approximate volume of solids which precipitate from the distillate upon cooling to 25° C. The results obtained are calculated in percentages by volumes and weights to tenths of 1 per cent., and reported as follows :—

Distillate.	Per cent. by volume.	Per cent. by weight.
1. Water or ammoniacal liquor . .	—	—
2. First light oils to 110° C. . .	—	—
3. Second light oils, 110° C. to 170° C.	—	—
4. Middle oils, 170° C. to 270° C. .	—	—
5. Heavy oils, 270° C. to 300° C. .	—	—
6. Pitch residue	—	—
Total	100·00%	100·00%

The above is applicable only to tars which are water free. In distilling crude tars, or tars which are contaminated with water, it is necessary to dehydrate them before submitting them to the regular distillation.

VALUE OF DIMETHYL SULPHATE TEST AFTER DISTILLATION AND FURTHER FRACTIONING

The dimethyl sulphate test is employed to detect the presence of petroleum or asphalt products in tar. Tar distillates are soluble in the dimethyl sulphate, while petroleum and asphalt distillates are not.

Dimethyl Sulphate Test

Method.—The residue (above 300° C.) obtained from the distillation test is used. This residue, after being cooled and weighed, is again distilled. Fractions are taken at 350° C. and 375° C. The fraction between 270° C. and 300° C., previously obtained in the distillation test, is now taken, and separately stirred, and, if necessary, heated to dissolve solids which may be present. The same thing is done with the 350° C. and the 375° C. fractions just obtained.

Four cubic centimetres of each of the three fractions are now poured separately into each of the three small 10-c.c. cylinders, and 6 c.c. of dimethyl sulphate are poured into each cylinder. The three are thoroughly shaken, and then allowed to rest for thirty minutes. After this period, if any petroleum or asphalt is present, there will appear a supernatent layer of insoluble oil in each cylinder. The amount of this oil can be read and calculated as to its percentage by volume of the sample of distillate taken. The results should be reported, as follows :—

Fractions.	Per cent. of distillate.	Per cent. of distillate insoluble in dimethyl sulphate.
270° to 300° C. .	—	—
300° to 350° C. .	—	—
350° to 375° C. .	—	—

Determination of Crude Tar Acids

Object.—As the naphthalene and the crude tar acids (phenols) are highly volatile constituents of the tar, their presence in the material as supplied for road construction is undesirable, inasmuch as it would imply a great deal of hardening of the tar under service. Thus, the British Standard Specifications for No. 1 Tar for Road Purposes provides that the tar shall not yield more than 3 per cent. by volume of tar acids, while the Specification for No. 2 Tar provides for not more than 2 per cent. These specifications provide also the total exclusion of crystal or solid matter in the middle oils (between 170° C. to 270° C.), when these oils are maintained at 30° and 25° C. for 30 minutes.

Method.—Warm the middle oils, distilling between 170° C. and 270° C., to about 30° C. in a measuring cylinder. Weigh a flask of 150 c.c. capacity ; pour 100 c.c. of the middle oils in it, and weigh again. The difference gives the weight of 100 c.c. of the middle oils. Warm the oils in the flask to 40° C. or 50° C. ; add to them 30 c.c. of solution of caustic soda, having a specific gravity of about 1·2, shake the mixture vigorously, and keep it at 40° or 50° C. for 15 minutes. Then shake the mixture again vigorously for a minute, pour it into a stoppered separating funnel, and allow it to rest therein until the solution of caustic soda has been separated from the oil. If the separation does not take place rapidly and distinctly it may be facilitated by adding 25 c.c. of benzole to the mixture. The soda solution free from oil is drawn off through the top of the funnel into a 100 c.c. measuring cylinder, and the oil is returned to the flask, and warmed and extracted by 20 c.c. of solution of caustic soda exactly as before. This soda solution is also drawn off into a 100 c.c. measuring cylinder, the contents of which are made slightly acid by the gradual addition, with gentle stirring, of hydrochloric acid. The crude tar acids separate and come to the top on standing, and their volume is read off on the scale of the measure. Since 100 c.c. of the middle oils were taken for the estimation, the reading gives directly the percentage of crude tar acids in the middle oils.

If n equals the volume of tar acids found, w the weight in grams of 100 c.c. of the middle oils, x the percentage (by weight) of middle oils in the tar, and s the specific gravity of the tar, then the percentage by volume of crude tar acids in the tar is :—

$$\frac{nxs}{w}$$

If 100 c.c. of middle oils is not available for the estimation, a smaller measured volume may be taken, and the quantities of soda solution used reduced in proportion. The necessary modification of the calculation of the result can be readily made.

PYRIDINE

The specification issued by the German Federal Council for testing rectified pyridine bases is as follows :—

Water.—This must be under 10 per cent. (it is often required that the water be not over 7 per cent.). The determination is carried out as follows : Into a special burette (see Fig. 148) 23 c.c. of 80° Tw. caustic soda, which must be perfectly clear, are carefully run, and if necessary after standing a short time adjusted. On to the top of the soda 25 c.c. of the pyridine bases to be tested are placed, a cork inserted into the neck of the burette and the contents gently shaken, after which they are allowed to stand for a short time, to separate. The increase in the volume of caustic soda indicates water.

Distillation.—Not less than 90 per cent. should distil over up to a temperature of 140° C. when 100 c.c. of the bases are distilled in a Wurtz distillation flask, the bulb of the thermometer being opposite the outlet tube.

Colour.—This must not be darker than a solution of 2 c.c. of N/10 iodine solution in one litre of distilled water.

Solubility.—The sample must be completely miscible in water to a clear solution. When 20 c.c. of the bases are mixed with 40 c.c. of water there should be no separation of oily drops.

Ammonia.—This must be absent.

The bases are required to answer the following test: 10 c.c. of a 1 per cent. (by volume) solution of bases must give a white precipitate with 5 c.c. of Nessler's solution.

Cadmium Chloride Test.—Ten c.c. of 1 per cent. (by volume) solution of the pyridine bases when mixed with 5 c.c. of 5 per cent. aqueous solution of anhydrous cadmium chloride and shaken vigorously should, almost immediately, yield a distinctly crystalline precipitate.

Titration Test.—To 1 c.c. of the bases dissolved in 10 c.c. of distilled water, N/1 H_2SO_4 is added from a burette until a drop of the mixture gives a distinct blue colour or border on congo paper. At least 10 c.c. of acid must be required. The congo paper is prepared by soaking filter paper in a one per thousand solution of congo red, and allowing to dry at ordinary temperature. The paper should be prepared just before the titration is carried out.

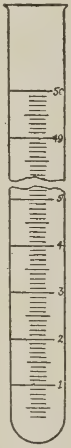

FIG. 148.—BURETTE FOR TESTING PYRIDINE FOR WATER.

In the new specification for pyridine bases the distillation requirements vary from those just given, thus: Up to 140° C. the bases should yield 50 per cent. and up to 160° C. 90 per cent. The titration test is carried out in the same manner, but 1 c.c. of the bases dissolved in 10 c.c. of water should require at least 9·5 c.c. of N/1 H_2SO_4.

Test for Oil in Crude Pyridine.—About 250 c.c. of the sample are dried with 80° Tw. caustic soda. Of this dried pyridine bases 100 c.c. are taken and distilled in a Wurtz flask until 10 c.c. have come over. To this volume 90 c.c. of distilled water are added and the lot shaken. If the solution becomes turbid oil is indicated. In this case a further 10 c.c. are distilled over into another measure and 90 c.c. of distilled water added. After mixing, should the solution become turbid, then the batch is rejected as unsuitable and requiring further treatment.

Valuation Test of Crude Pyridine

Water.—This is carried out in the manner described under German specification for rectified bases (page 422).

Distillation.—Two hundred and fifty c.c. of the sample are dried by shaking with three separate quantities of 80° to 90° Tw. caustic soda, the volume in each case being about 100 c.c. The dried pyridine is measured, and then placed into a 300 c.c. round-bottomed distilling flask, to which is fitted a le Bel Henninger fractionating head. This head should be provided with three bulbs, and have an overall length of about 20 inches, the distance between the bottom of the head and the outlet of the delivery tube being approximately 13 inches. The fractions are collected as follows: From drop to 140° C. (refined pyridine); from 140 to 160° C. (heavy refined pyridine); from 160 to 180° C. (heavy bases). The refined pyridine fraction is tested for (*a*) water; (*b*) oiliness; and (*c*) percentage of distillate at 140° C. Methods of carrying out these tests have already been described.

Estimation of Pyridine in Naphthas, etc.

Rough Method.—Into a 100 c.c. stoppered test mixer 50 c.c. of dilute sulphuric acid (1 : 2) are placed. On to this are run 50 c.c. of the oil to be tested, the stopper inserted, and the contents well shaken and allowed to settle. The decrease in the volume of the oil or the increase in that of the acid indicates the amount of pyridine contained in the 50 c.c. of oil.

A more Accurate Method.—Take 500 c.c. of the naphtha, place in a separating funnel and wash with 20 per cent. of diluted B.O.V. (1 acid 2 water) in two lots of 40 c.c. and one of 20 c.c. Carefully separate the acid extracts, bulk them, place in a steam distillation apparatus, make alkaline with 40° Tw. caustic soda, and then steam distil until about one-third of the original bulk in the distilling flask has been collected. Place this distillate in a separating funnel and add 90° Tw. caustic soda until no more oil separates, allow to rest, carefully run off the subnatant alkaline liquor, dry the pyridine bases with a little 90° Tw. caustic soda, separate most of the alkali and then run the remainder with the bases into a narrow measuring tube, rinse out the funnel with a little 90° Tw. caustic soda into the tube, allow to rest, and read off volume of pyridine bases.

The following is a delicate test for pyridine[1]: If a few drops of aniline are added to a solution of pyridine containing water and a trace of freshly prepared cyanogen bromide, a red colour is immediately obtained and crystals of *a*-anilidophenyldihydropyridine bromide separate. Pyridine can be thus detected at a dilution of 1 : 350,000.

BENZOLE

Specific Gravity.—This is determined with an ordinary specific gravity hydrometer after cooling the benzole to 15·5° C. Some chemists take the gravity at the temperature of the laboratory and correct it by adding ·001 to the specific gravity reading for every 2° F. above 60° or subtracting the same figure for every 2° F. below 60°. This method is not to be recommended, as the factor is not accurate for all temperatures. The best method of estimating the specific gravity of this material is to use the Regnault specific gravity bottle.

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[1] F. Lehner, *Chem.-Zeit.*, 1922, 46, 877. See also *J.S.C.I.*, November 15th, 1922, Vol. 41, No. 21, p. 852 A.

Distillation.—For making rough works tests, such as determining the percentage given off from a sample obtained from the worm end of the benzole still, an 8-oz. retort is used, connected to a Liebig condenser and supplied with a benzole testing thermometer, which is graduated from 70° to 130° C. in one-fifth of a degree. The length of the Liebig condenser is about 30 inches and the condenser tube about 1 inch wide. The thermometer is fixed so that the bottom of the bulb is about $\frac{3}{8}$ inch from the bottom of the retort. A Rose burner is used to heat the contents of the retort, and the distillation should proceed at the rate of about two drops per second. It should be added that benzole is tested before delivery for its percentage at 100° C. or 120° C., according to quality, in the same apparatus.

Pyridine in Benzole.—Badly made benzoles may contain pyridine bases, and it is advisable to test for these if the sample is suspected. The test may be carried out as follows: One hundred c.c. of benzole are agitated with four parts of a 10 per cent. solution of sulphuric acid in a separatory funnel. After a thorough shaking, the contents of the funnel are allowed to rest and the acid solution run off from the bottom into a distilling flask and then made alkaline with caustic soda. The flask is connected up to a Liebig condenser and a steam-generating apparatus, and the contents submitted to steam distillation until about one-third of the volume in the distilling flask has come over. When the distillate is cold 90° Tw. caustic soda is added, and the bases which rise to the surface, if sufficient, are carefully separated and measured.

Total Sulphur in Benzole.—The following method, if carefully conducted, will give very satisfactory results. It is a modification of a test published by Irwin. Into a 2-oz. spirit lamp provided with the usual unplaited wick, which is kept very short on the burning side, are placed 2 c.c. of benzole which should be measured in from a burette at 60° F. On the top of the benzole are poured 20 c.c. of 90 per cent. alcohol B.P., and the lot carefully mixed. The spirit lamp is placed under the trumpet stand of the Metropolitan Gas Referees' sulphur test apparatus, the burner portion projecting through the centre hole where in the ordinary course the gas burner should be. The Gas Referees' apparatus is prepared in the same fashion as when determining the sulphur in a sample of coal gas; that is, a little powdered ammonium carbonate is sprinkled over the top layer of glass marbles in the condenser and a few small lumps placed round the burner top. The lamp is lit immediately it is placed under the trumpet and allowed to burn at such a rate that it will take about $1\frac{3}{4}$ hours to consume the contents. Immediately the lamp goes out it is removed, and a further 5 c.c. of alcohol placed in it, and this burnt under the apparatus until the lamp goes out, the time taken being about 20 minutes. The flame should be almost colourless at the end of the process. The whole of the apparatus is washed down with distilled water in the usual fashion into a beaker, and the sulphur estimated in the usual way and if desired calculated to CS_2. To do this is not strictly correct, as CS_2 is not the only sulphur compound present in commercial benzoles. There are ways of estimating CS_2 in benzole, such as the phenylhydrazine test and the copper xanthate method. The reader is referred to *Allen's Commercial Analysis* and other authorities on analytical matters for these tests and also to p. 427.

Estimation of Fatty Hydrocarbons.—This test is sometimes applied to benzole, especially when it is intended for the manufacture of nitro-compounds. Lunge gives the following process :

"Place 100 c.c. of benzene, or benzole, in a flask of about 500 c.c. capacity, provided with a dropping funnel, and a long tube for condensing any hydrocarbon volatilizing. Prepare also a mixture of 150 g. nitric acid of specific gravity 1·4, and 180 or 200 g. sulphuric acid, specific gravity 1·84, which must be allowed to cool before use. Run this, drop by drop, through the top funnel into the benzole, shaking this up almost constantly. As soon as the temperature rises, cool the flask by immersing it in a dish full of water. When all the acid has been added, and when no further rise of temperature takes place spontaneously, heat the flask gently for an hour or two (during this time the glass reflux tube is best replaced by a proper reflux condenser). Allow the whole to settle, and separate the lower acid layer by means of a separating funnel from the crude nitrobenzene. Dilute the acid with several times its bulk of water ; any oily liquid separating after a few hours' rest is added to the nitrobenzene. Wash the crude nitrobenzene three times with its own bulk of water, once with a very dilute solution of caustic soda (if a concentrated solution is employed, an emulsion is formed which is very awkward to manage), and again with water, taking care that no oil is lost in separating the washings. The well-settled liquor can be at once tested for its specific gravity, which, in the case of 90 per cent. benzole, ought to be 1·20 ; with 50 per cent. benzole, 1·19 at 15° C. ; but this is not decisive, as the nitrobenzene is not quite free from water, and some benzole may have escaped nitrification, the liquor is therefore distilled from a fractionating flask till the temperature has reached 150° C., and the distillate is once more nitrated, but this time with large excess of the acid mixture ; anything remaining undissolved may be regarded as non-nitrifiable hyrocarbons. Theoretically, 100 parts of benzene furnish 157·6 of nitrobenzene ; 100 parts of toluene, 148·9 of nitrotoluene."

Paraffins in Commercially Pure Benzene or Toluene

A rough method of estimating paraffins in these materials is to first wash out the carbon disulphide from the sample, then dry with a small quantity of granular calcium chloride, and finally determine the specific gravity at 15° C. Should the sample under examination be a benzene then for each 0·001 that the specific gravity is below 0·873, reckon 1 per cent. of paraffins, and should it be a toluene then for each 0·001 below 0·870 allow 0·667 per cent. of paraffins.

The carbon disulphide may be removed from the sample by shaking with a pure alcoholic solution of caustic potash or caustic soda, allowing to stand an hour or two and then removing the potassium or sodium xanthate formed by washing repeatedly with small quantities of water.

A useful paper on the "Determination of aromatic hydrocarbons in mixtures of hydrocarbons," by H. T. Tizard and A. G. Marshall, appeared in the *Journal of the Society of Chemistry* for February 15th, 1921, pages 20T to 25T.

Determination of Carbon Disulphide in Benzole

Kraemer and Spilker use the following method : A solution of alcoholic potash is prepared by dissolving 22 grams of pure caustic potash in 180 grams of absolute alcohol. Fifty grams of this solution are mixed with 50 grams of benzole, and the mixture is allowed to remain at the ordinary temperature for several hours. Then about 100 c.c. of distilled water are added to the mixture, the lot well shaken, and the aqueous liquor allowed to separate. This process is repeated several times (about 4) and the aqueous solutions mixed. The potassium xanthate dissolved in the mixed washings is estimated by titration with a solution of copper sulphate containing 12·475 grams of the crystalline salt per litre. The method of procedure is as follows : The whole of the xanthate solution, or an aliquot part, is first neutralised with acetic acid and the standard copper solution is then added slowly until a drop removed by a glass rod and placed on a piece of filter paper beside a drop of potassium ferrocyanide solution produces a red colour at the point of contact. The approach of the end of the reaction is indicated by the coagulation of the cupric xanthate precipitate. The calculation is based upon the fact that each 1 c.c. of the copper sulphate solution is equivalent to 0·0076 gram of carbon disulphide.

For another method of determining carbon disulphide the reader is referred to a paper by P. E. Spielmann and F. Butler-Jones on the "Estimation of Carbon Disulphide."[1]

Thiophene in Commercial Benzoles

A. Meyer[2] recommends the following process : 5 c.c. of the benzole to be examined are mixed in a stoppered bottle, with 75 c.c. of methyl alcohol, and 20 c.c. of reagent made as follows : mercuric oxide 50 grams, dissolved in 200 c.c. of sulphuric acid, and then diluted with 1,000 c.c. of water.

The benzole reagent mixture is shaken from time to time for 30 minutes, and is then filtered. Ten c.c. of the filtrate are diluted with 20 c.c. of water, a few drops of nitric acid and 1 c.c. of a 20 per cent. solution of iron ammonium alum added, and the mixture then titrated with N/10 ammonium thiocyanate solution. On account of the possible presence of acetone in the methyl alcohol, it is necessary to make a blank test, using 5 c.c. of benzene free from thiophene. The calculation is as follows : $0{\cdot}01 \times 2{,}000 \times (n\text{-}n_1) \times 0{\cdot}14$, where n equals the blank titration and n_1 the titration on the sample under examination. The calculation gives the amount of thiophene in 1 litre of benzole.

Another test for Thiophene is as follows : To 2 c.c. of benzole are added 20 c.c. of Denigés' reagent (20 c.c. of concentrated sulphuric acid are added to 100 c.c. of water, and 5 grams of mercuric oxide are dissolved in the acid solution) and the mixture shaken for six hours. If thiophene is present a white precipitate is formed, and this is separated by filtering through a tared Gooch crucible and then washed with hot water until quite neutral, dried carefully in an air oven at 110°–115° C., cooled in a desiccator and then weighed. The weight of the precipitate multiplied by 0·0758 will give the amount of thiophene contained in the 2 c.c. of benzole.

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[1] *J.S.C.I.*, 1919, 38, 185–188T.

[2] *Comptes rend.*, 1919, 169, 1402, 1404.

Government Specification for Pure Benzole

Appearance.—To be a clear water-white liquid free from suspended solid matter.

Specific Gravity.—The specific gravity is to be not less than 0·883 and not more than 0·887 at 15·5° C.

Boiling-Point.—Must correspond approximately to 80·5° C. corrected.

Sulphuric Acid Test.—90 c.c. of the benzole shaken with 10 c.c. of 90 per cent. sulphuric acid for five minutes should impart only a slight colour in the acid layer.

Distillation Test

Apparatus.—A fractionating flask of 200 c.c. capacity fitted with thermometer graduated to read to one-tenth of a degree Centigrade and so adjusted that the top of the bulb is on a level with the side tube. The flask to be placed on a sheet of asbestos board having a hole 1-inch in diameter in the centre, in which the bottom of the flask rests, the bulb being surrounded by a cylinder of wire gauze resting on the asbestos sheet, and of such a height that the top of the cylinder is on a level with the top of the bulb.

Distillation.—100 c.c. of the benzole are placed in the fractionating flask and heated by a small flame on the portion of the flask exposed by the hole in the asbestos sheet, the distillation being conducted at such a rate that the distillate passes from the condenser into a 100 c.c. graduated cylinder at the rate of about 7 c.c. per minute. The temperature is read when 5 c.c. and again when 95 c.c. have collected in the receiving cylinder. The difference between the two readings must not be greater than 0·5° C.

NATIONAL BENZOLE ASSOCIATION'S SPECIFICATION FOR BENZOLE FOR USE AS A MOTOR SPIRIT

1. Specific Gravity : 0·870 to 0·885.
2. Distillation Test (by flask) : Benzole shall give a distillate of not less than :

75	per cent.	at	100° C.
90	,,	,,	120° C.
100	,,	,,	125° C.

3. Sulphur : The total sulphur shall not exceed 0·40 per cent.
4. Water : The benzole shall be entirely free from water.
5. Colour : Water-white.
6. Rectification test : 90 c.c. of the sample shaken with 10 c.c. of 90 per cent. sulphuric acid for 5 minutes shall not give more than a light brown colour to the acid layer.

7. Purity: Benzole shall be entirely free from acids, alkalis and sulphuretted hydrogen.

8. Freezing: Benzole shall not freeze until below 7° F. (25 degrees of frost).

Benzene for intermediate Manufacture.—Commercially pure benzene for use in the manufacture of intermediates should, when distilled, all come over within one degree of the boiling-point of the chemically pure product. It should solidify when cooled below 0° C. When shaken with concentrated sulphuric acid, the acid should only darken slightly, and a blue colour should not develop on shaking with concentrated sulphuric acid and a tiny piece of isatin. If agitated with a few drops of phenylhydrazine and then allowed to stand, a crystalline precipitate must not appear. When nitrated—see page 426—and then steam distilled only a very small quantity of non-nitrifiable hydrocarbons of the paraffin series should be obtained.

VALUATION OF CRUDE NAPHTHA FOR YIELD OF BENZOLE, ETC.

Crude naphtha and crude benzole are examined for the yield of light products in the chemical laboratory by the following method: Five hundred c.c. of the oil are placed in a distilling flask fitted with a 5-bulb Glinsky or le Bel Henninger distillation head. The delivery tube of this latter piece of apparatus is connected up to a Liebig condenser. Distillation is commenced and the amount of distillate which comes over below 200° C. is collected and the percentage read off. This distillate is then washed, first with about 60 c.c. of 60° Tw. caustic soda, using a separating funnel. The alkaline liquor which separates is carefully removed and the shrinkage in the oil carefully measured. The oil is then washed once or twice with water, care being taken, of course, to prevent loss of oil when separating the water, and then agitated with B.O.V. of about 140° Tw., two washes of $2\frac{1}{2}$ per cent. being given. The acid liquor which separates is carefully removed, and the oil then given one or two water washes, after which it is washed with 50 c.c. of 20° Tw. caustic soda and then with one wash of water. It is then allowed to rest to separate the last traces of water, and the shrinkage of oil carefully measured. The entire quantity of the washed oil is now placed into a distilling flask fitted with a Glinsky or le Bel Henninger head, as just described, and the following fractions are collected:

Drop to 100° C. equals 90's benzole.
100 ,, 120° C. ,, 50's–90's benzole.
120 ,, 160° C. ,, solvent naphtha.
160 ,, 190° C. ,, heavy solvent.

The bottoms are also measured. It should be added that the volumes of these fractions will give only an approximate idea of what is obtained in the works, but at the same time they form a useful guide when buying, say, crude benzole or crude naphtha.

In the case of crude naphtha the percentage at 120° C. is often determined by using a retort and condenser as just described under benzole tests, and, of course, the specific gravity is always taken. It is advisable to test the crude naphtha for tar acids and basic bodies by the methods already given.

NAPHTHAS

Distillation.—The various qualities of naphtha are tested in a similar apparatus to that used for benzole, whether it is required to control the working of the naphtha still or the quality of the products to be offered for sale. A special thermometer is used, graduated from 90° to 200° C. in half degrees, and this is placed in the retort in a similar position to that occupied by the benzole thermometer. The drop point and the percentage at 160°, 170° or 200° is read off according to the quality of the naphtha.

Specific Gravity.—This is taken by a hydrometer or in the Regnault specific gravity bottle.

Flash Point.—This is determined in the Abel test apparatus, in a similar fashion to that used for the determination of the flash-point of petroleum.

Pyridine Bases and Tar Acids.—It is advisable to examine solvent naphthas for pyridine bases and also for tar acids. The latter substances are estimated as already described (see page 391), and the former (unless suspected to be present in more than traces, when the test described under benzole is used) by the following method, which is known as the Weber test for pyridine: Shake out 100 c.c. of solvent naphtha with 100 c.c. of distilled water in a separating funnel. Take about 15 c.c. of the water extract and add to it 1 c.c. of a 10 per cent. solution of copper sulphate. Bring the mixture to boiling-point. It is required that no turbidity occurs. According to Weber, if the mixture remains clear the solvent naphtha is free from pyridine, or the amount it contains does not reach more than one part in 1,500 parts of solvent naphtha. A very faint turbidity after standing 30 minutes will be equivalent to approximately ·06 per cent., and a pronounced bluish white turbidity to 0·1 per cent. If the quantity of pyridine exceeds 0·1 per cent. a copious precipitate results, and should 0·3 per cent. be present a dense precipitate is at once produced. If the solvent naphtha be required for rubber works, this test often has to be used, and also the following: 25 c.c. of R.O.V. and 75 c.c. of the solvent naphtha are placed in a stoppered and graduated test mixer. The mixture is well agitated and allowed to rest. The R.O.V. should not increase in bulk more than 4 c.c., making a total of 29 c.c., and the colour should not be more than a deep orange.

Another test often used for pyridine is to extract 50 c.c. of the solvent naphtha with 50 c.c. of B.O.V. in a separating funnel, allow to rest, separate the acid extract, neutralise with fairly concentrated caustic soda, say 60° Tw., and see whether pyridine can be detected by the sense of smell.

VALUATION OF LIGHT OIL, ETC.

There are several methods of testing light oil in order to obtain an idea of the yield of light products which may be expected in the works. One of the methods is the following: Five hundred c.c. of the light oil are placed in a distillation flask fitted to a 5-bulb Glinsky or le Bel Henninger distillation head and Liebig condenser. The flask is heated with a Bunsen burner, and all the distillate which comes over below 200° C. collected and the percentage read off. This distillate is washed first with about 60 c.c. of 60° Tw. caustic soda, and then once with about the same volume of clean water, after which the loss, due to the alkaline wash, is carefully measured and the percentage noted. It is now washed with 5 per cent. of B.O.V. in two $2\frac{1}{2}$ per cent. quantities, and then three times with about 60 c.c. of water, after which an alkaline wash is given, using about 50 c.c. of 20° Tw. caustic soda, and finally a wash with 50 c.c. of clean water. The loss in volume of oil is carefully measured, and the washed distillate is then placed in a distillation flask and distilled up a fractionating head, using one or other of the types just mentioned, and the following fractions collected :

1. Drop to 100° C. equals 90's benzole.
2. 100° ,, 120° C. ,, toluole.
3. 120° ,, 160° C. ,, solvent naphtha.
4. 160° ,, 185° C. ,, medium heavy naphtha.
5. 185° ,, 200° C. ,, heavy naphtha.

The results are calculated on the original oil and tabulated as follows :

Distillate above 200° C.	per cent.
Loss by soda and water washing . .	,,
Loss by acid, soda and water washing .	,,
90's benzole	,,
Toluole	,,
Solvent naphtha	,,
Medium heavy naphtha	,,
Heavy naphtha	,,

Specific Gravity.—This is taken by one of the methods already described.

Tar Acids and Pyridine Bases.—The processes for estimating these substances have been described already.

BRITISH STANDARD SPECIFICATION FOR BENZOL FOR MOTOR FUEL

(Commonly known as Benzole)

The following British Standard Specification No. 135 for benzol for motor fuel (commonly known as benzole),[1] is reprinted by permission of the British Engineering Standards Association.

Definition

1. The term " Benzole " shall denote a liquid consisting essentially of a mixture of benzene and not more than 30 per cent. by volume of toluene and xylenes.

Description

2. The material shall be a clear " water-white " liquid free from undissolved water and other visible impurities (see Appendix I).

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[1] Official copies of this Specification can be obtained from the Secretary of the Association, 28 Victoria Street, London. Price 1*s.* 2*d.* net, post free.

Specific Gravity

3. The specific gravity at 15·5° C. (60° F.) shall be not less than 0·870 and not more than 0·885.

Distillation Range

4. When 100 c.c. of the material are distilled in the Standard Distillation Apparatus (B.S. Specification, No. 2 D. 15; see Appendix VII), at a rate of 7 c.c. per minute, there shall distil at 760 mm. pressure

Not less than 60 c.c. at or below 90° C. (194° F.)
,, ,, 75 c.c. ,, ,, 100° C. (212° F.)
,, ,, 90 c.c. ,, ,, 120° C. (248° F.).

The flask shall be dry at a temperature not exceeding 125° C. (257° F.). The temperature recorded by the thermometer shall be corrected for emergent stem and barometric pressure by means of the formulæ given in Appendix II.

Residue

5. The amount of non-volatile residue remaining when 20 c.c. of the material are evaporated, and subsequently heated for two hours on a water bath at 100° C. (212° F.), shall not exceed 0·01 per cent. by weight.

Coloration with Sulphuric Acid

6. The coloration imparted to pure sulphuric acid (90 per cent. H_2SO_4), free from nitric acid, when 90 c.c. of the material are shaken with 10 c.c. of the acid for five minutes at ordinary temperatures shall be not more than a light brown.

Sulphur Content

7. The total sulphur content shall not exceed 0·4 per cent. by weight. A convenient method for the estimation of sulphur is given in Appendix III.

Freedom from Acid and Alkali

8. The material shall give no reaction for free acid or free alkali when tested by the method described in Appendix IV.

Freedom from Sulphuretted Hydrogen

9. The material shall give no reaction for sulphuretted hydrogen when tested by the method described in Appendix V.

Freezing-Point

10. The freezing-point shall be not higher than −14° C. (7° F.) when determined by the method described in Appendix VI.

APPENDIX I

METHOD FOR TESTING COLOUR

One hundred c.c. of the material shall be placed in a clean, dry Nessler cylinder and compared with 100 c.c. of distilled water in another Nessler cylinder, both cylinders being placed on a sheet of white paper or on a white porcelain tile.

APPENDIX II

TEMPERATURE CORRECTIONS FOR EMERGENT THERMOMETER STEM AND BAROMETRIC PRESSURE

(a) *Emergent Thermometer Stem.*—The number of degrees Centigrade to be added to the thermometer reading shall be calculated as follows :—

Let t be the number of degrees Centigrade to be added.
t_0 be the thermometer reading.
t_1 be the air temperature in degrees Centigrade half-way up the exposed thread of mercury.
N be the number of degree Centigrade divisions on the scale exposed.

Then :

$$t=0{\cdot}000143\ (t_0-t_1)\ N$$

and the corrected reading$=t_0+t$.

(b) *Barometric Pressure.*—The number of degrees Centigrade to be added to the thermometer reading shall be calculated as follows :—

Using the above notation and p=the observed barometric pressure in millimetres

Then :

$$t=0{\cdot}0001\ (273+t_0)\times(760-p).$$

APPENDIX III

METHOD FOR THE ESTIMATION OF SULPHUR

The following is a convenient method for the estimation of sulphur in benzole :—

The apparatus used is shown in Fig. 149, and consists of a U-tube C loosely packed with cotton-wool and suspended in the beaker B, which is partly filled with water. One arm of the U-tube is connected to one limb of a Y-tube D, the second limb of which is connected to the wash-bottle A.

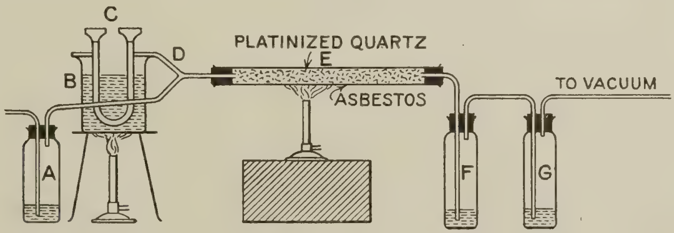

FIG. 149.—APPARATUS FOR THE ESTIMATION OF SULPHUR IN BENZOLE.

The third limb of the Y-tube leads into the tube E of clear silica, 15 inches long by ½ inch internal diameter, which tube is almost completely packed with small pieces of platinised quartz.[1] The outlet tube of E is connected with wash-bottles

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[1] The quartz consists of small pieces of semi-transparent, partially devitrified quartz, platinised by immersion in a 5 per cent. solution of platinum chloride, pouring off the excess of solution, drying and igniting. Platinised asbestos must not be used.

F and G, containing sodium hypobromite solution. A vacuum service is connected with G so that a current of air may be drawn through the apparatus.

To perform the analysis the silica tube is heated to redness for a length of about four inches.

The taps of C are opened and the vacuum adjusted to give a steady stream of air through the apparatus. The tap on C nearer the silica tube is then closed, and that further from the tube removed, and 2 c.c. of the benzole under examination rapidly run into C from a standardised pipette. The tap is then quickly replaced in the open position, and the tap nearer the silica tube opened slightly. As soon as benzole vapour begins to be drawn through by the vacuum the platinised quartz begins to glow brightly. The air passing through A is adjusted until the reaction is steady. The combustion is allowed to go on until the glow on the platinised quartz dies down with the taps on C full open. The water in the beaker is then heated to boiling, and the combustion proceeded with until all the benzole has been oxidised. In a well-conducted experiment the total time taken for this operation should be not less than twenty and not more than forty-five minutes.

The contents of F and G are then washed into a beaker, acidified with HCl, heated to boiling until all bromine is expelled, and slight excess of barium chloride added. The contents are allowed to stand over night, filtered and the $BaSO_4$ ignited and weighed.

Then :

$$\text{Percentage of sulphur in the sample} = \frac{(\text{weight of } BaSO_4) \times (0{\cdot}1377)}{(\text{specific gravity of sample}) \times (2)}$$

The sodium hypobromite is prepared by shaking 8 c.c. of bromine[1] with 1 litre of 10 per cent. caustic soda solution, 100 c.c. of solution being used for each analysis. As no commercial caustic soda or bromine is free from sulphur compounds, a " blank " must be performed for each preparation of solution.

APPENDIX IV

Method of Testing for Free Acid or Free Alkali

Fifty c.c. of the material shall be shaken in a clean stoppered vessel with a little water and a drop of methyl orange solution as indicator. The colour of the aqueous layer shall be neither a distinct red nor a distinct yellow.

APPENDIX V

Method of Testing for Sulphuretted Hydrogen

Fifty c.c. of the material shall be shaken in a clean stoppered vessel with a small quantity of a solution of lead acetate. The lead acetate solution shall not become coloured.

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[1] The bromine used must be as pure as possible. Some of the bromine obtainable on the market is heavily contaminated with sulphur compounds.

APPENDIX VI

METHOD OF DETERMINING THE FREEZING-POINT

About 15 c.c. of the material shall be placed in a clean, dry, wide test tube containing a thermometer. The test tube shall then be immersed in a suitable freezing mixture and its contents frozen practically solid. The test tube shall then be removed from the freezing mixture, wiped clean and dry, and the temperature noted at which the crystals nearly disappear, the contents of the tube being well stirred with the thermometer while the crystals are melting.

APPENDIX VII

STANDARD DISTILLATION APPARATUS

1. *Description.*—The apparatus is shown in Figs. 150 and 151. It consists of the following parts :—

(*a*) A distillation flask A of the dimensions shown in Fig. 150, fitted with a thermometer B with its bulb just below the exit tube of the flask, the thermometer B being graduated in single degrees and being preferably of such a length that the column of mercury in the stem is completely surrounded by the vapour of the boiling liquid.

(*b*) A cylindrical metal wind screen D divided by a diaphragm C of soft asbestos millboard 6 mm. thick having a circular hole 5 cm. diameter in the centre, the support for the asbestos diaphragm being such that the diameter of the hole therein is greater than that in the asbestos diaphragm. The lower portion of the screen is provided with draught holes and mica windows for observing the flame ; the upper portion has a slit to admit the side tube of the flask, and another for viewing the thermometer ; the top is not to be closed by a lid.

(*c*) A burner E with an adjustable gas tap.

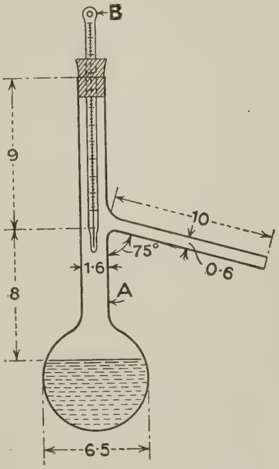

FIG. 150.—STANDARD DISTILLATION FLASK.

(Dimensions are given in centimeters).

(*d*) A glass condenser F of the dimensions shown in Fig. 151. Instead of the outlet of the condenser being bent, an adaptor may be used.

(*e*) Receiver G, consisting of a measuring flask or a graduated measuring cylinder.

(*f*) A pendulum H is a convenient adjunct for measuring the rate of distillation.

2. *Method of Using Apparatus.*—

(*a*) 100 c.c. of the liquid to be tested shall be put into the flask and a few small pieces of clean porous pot added.

(*b*) The cork and thermometer shall be introduced *and the flask pressed on to the asbestos diaphragm.*

(*c*) The burner shall be lighted and the flame so regulated that the specified rate of distillation is obtained, the distance between the burner and the bottom of the flask being so adjusted that only a minimum flame is necessary.

(*d*) The temperature shall be noted when the first drop falls into the receiver, and after definite amounts have distilled, in accordance with the requirements of the specifications.

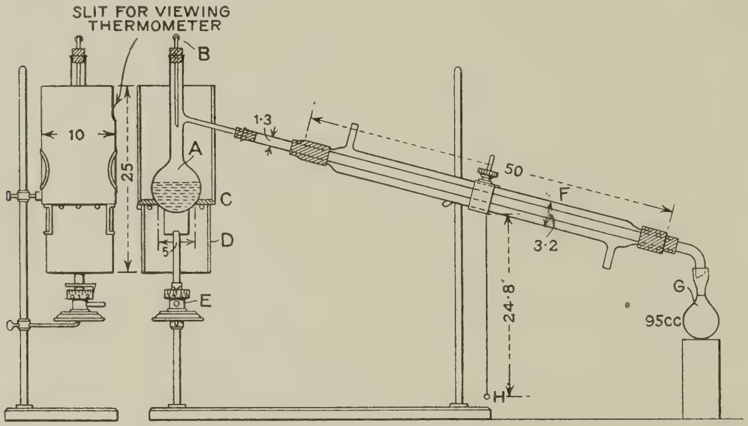

FIG. 151.—STANDARD DISTILLATION APPARATUS.
(Dimensions are given in centimeters.)

TOLUENE

According to John Scott Lumsden,[1] commercial toluene contains varying amounts of a liquid which cannot be nitrated and has to be distilled off with the toluene during rectification. This liquid has not been isolated and it is assumed that it is a paraffin mixture which boils close to the boiling-point of toluene. This author carried out work upon commercial toluene for the purpose of finding some easily applied method for estimating the degree of purity and came to these conclusions (1) that the specific gravity of commercial toluene gives a fair indication of the amount of impurity present; and (2) the estimation of the temperature of miscibility with acetic acid is quickly done, and, although a comparative method, if skilfully carried out, is trustworthy. A nitration and estimation of the excess of nitric acid by the nitrometer is believed to be the most accurate test and indicates the total nitration which has taken place, and the weighing of the solid after nitration gives the actual practical yield of nitro-compound. By none of the methods under ordinary conditions of working can an accuracy closer than ½ per cent. be expected.

A given sample of commercial toluene will have a gravity of approximately 0·872 at 15° C., and Lumsden finds that the presence of 1 per cent. of paraffin produces a lowering of the density of 0·0013. This figure, of course, can only be approximately correct; if the toluene examined contains a type of paraffin boiling at between 108 and 112° C., other impurities may destroy the accuracy completely.

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[1] "Criteria of the Degree of Purity of Commercial Toluene." *J.C.S.*, 686, December, 1919, pp. 1366–1372.

Government Specification for Pure Toluole

Specific Gravity.—The specific gravity is to be not less than 0·868 and not more than 0·870 at 15·5° C.

Boiling-Point.—Must correspond approximately to 110° C. corrected.

Appearance, Sulphuric Acid Test, and Distillation Test correspond to those given for Pure Benzole (see page 428).

Toluene for intermediates.—On shaking commercial toluene for use in the manufacture of intermediates, with concentrated sulphuric acid it should not become more than slightly darkened; upon distillation the whole should come over within one degree, between 111°–112° C.

Xylene for intermediate manufacture.—Commercial xylene (which is a mixture of o-, m-, and p- xylenes) for use in the manufacture of intermediates must be practically free from paraffin hydrocarbons and it should possess a very short distilling range, for instance, between 136°–140° C.

The author is indebted to Dr. H. Colman and Mr. E. W. Yeoman, and also the Publications Committee of the Society of Chemical Industry for their kindness in allowing the following paper to be published in full.

DETERMINATION OF BENZENE, TOLUENE, ETC., IN COAL TAR AND SIMILAR PRODUCTS, AND IN THE INTERMEDIATE PRODUCTS OF TAR DISTILLATION

By H. G. Colman, d.sc., and E. W. Yeoman, b.sc.

During the past few years the authors have carried out a large number of tests of these products by methods of which sectional accounts have been published in some cases from time to time. Owing to the necessities of the time, it was found advisable to publish these sectional accounts without waiting for their extended investigation, and as further experience has resulted in various modifications and additions to these methods, a general account of them, and of the principles on which they depend, is given in the present paper.

The general aim of the investigation has been the elucidation of methods which would give results of reasonable accuracy with products of widely varying composition. Where the products to be analysed only vary in composition within moderate limits, simpler and shortened methods can be employed giving results of sufficient accuracy for many purposes, but where such methods are used on products differing widely in composition, they are apt to give results which with abnormal samples are far from accurate.

General Scheme of Analysis Adopted

By distillation of the various tars, and subsequent fractionation of the lower-boiling distillates after treating them with concentrated sulphuric acid and caustic soda to remove unsaturated hydrocarbons and phenols, the lighter tar constituents are separated into the following fractions: (1) Fraction up to 90° C., (2) 90°–140° C., (3) 140°–160° C., (4) 160°–200° C.

The first fraction "up to 90°," when the fractionation is carried out under specified conditions, contains the aromatic hydrocarbons benzene and toluene only, but may also contain carbon bisulphide and saturated paraffin hydrocarbons or naphthenes of similar boiling-point when these are present in the original tar or oil analysed.

The second fraction "90°–140°" contains only the aromatic hydrocarbons benzene, toluene, and the xylenes, together with paraffins or naphthenes of similar boiling-point if present in the tar.

The third fraction "140°–160°" contains chiefly the constituents of the "solvent coal-tar naphtha" of commerce, namely, xylenes, cumenes, and other benzene homologues boiling for the most part between 140° and 170°, and also any paraffins or naphthenes of similar boiling-point present in the original tar.

The fourth fraction "160°–200°" represents approximately the "heavy solvent naphtha" of commerce, and consists mainly of benzene homologues boiling at about those temperatures, with paraffins or naphthenes present in the tar.

Owing to the large number of the individual hydrocarbons present in each of the last two fractions, and to the small differences between the boiling-points of the various constituents, no determination of the relative amounts of each has been found practicable by distillation methods.

In the first two fractions, on the other hand, it is possible by simple distillation methods to ascertain with a considerable degree of accuracy the quantities of benzene, toluene, and the sum of the isomeric xylenes present, and to ascertain from specific gravity determinations the amounts of carbon bisulphide and paraffin or naphthene hydrocarbons present. The same methods can be employed for the analysis of commercial benzole and commercial toluole, which are in general similar in composition to the fractions "up to 90°" and "90°–140°" respectively.

Preliminary Distillation of the Tar or other Crude Oil

A known volume of the tar or oil is distilled from a metal still. (It is frequently more convenient to take a known weight of the tar or oil, and calculate the volume from the weight taken and the specific gravity of the sample.) The tar is then carefully distilled until the thermometer in the vapour shows a temperature of 230° C., to ensure that all the low-boiling constituents of the tar or oil are driven over into the distillate. In many cases, such, for example, as the benzolised oil resulting from the washing of coal gas with oil for benzole recovery, it is often more convenient to blow steam through the oil in the still when the thermometer indicates a temperature of 130°–140° C. and to continue passing the steam until about 100 c.c. of water has condensed in the receiver for each litre of tar or oil taken.

The distillate, after separation of water, is then redistilled from a round-bottomed glass or metal flask fitted with a Young 12-bulb pear fractionating column, or other efficient column of a form which drains almost completely, the rate of distillation being maintained as nearly as practicable at about 4 c.c. per minute.[1]

The distillation is continued until the thermometer at the head of the column shows a temperature of 200° C.; the volume of this distillate, less any water present, is then read off and its percentage of the original volume of tar calculated.

The quantity of tar or oil originally taken should be such that the amount of distillate to 200° thus obtained is at least 250 c.c. For greater accuracy a larger quantity is advantageous, but the time required for the test is considerably increased thereby.

In the case of a product which only contains up to 25 per cent. of constituents boiling above 200° C., such as the "crude benzole" recovered from coal gas by washing, 250–500 c.c. of this material is directly fractionated using a Young 12-bulb pear column, and the distillate to 200° collected, the preliminary distillation to 230° being omitted in such cases.

Purification of the Distillate to 200° *C.*

In order to purify the distillate, not less than 200 c.c., and preferably at least 250 c.c., is shaken with one-quarter of its volume of 10 per cent. aqueous caustic soda, allowed to settle, the caustic layer run off, and the oil washed with water, which is also run off, and the volume of residual oil measured. The loss of volume represents approximately the volume of tar acids in the volume of oil taken.

After alkali-washing, the remaining oil is shaken for 5 minutes with 8 per cent. of its volume of concentrated sulphuric acid and allowed to settle for 15 minutes.[2]

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[1] The usual method of specifying the rate of distillation in "drops per second" is unsatisfactory, as the size of the drop may vary at least threefold, according to the diameter, slope, and exact shape of the end of the condenser tubes. As the specification of "drops per second" is, however, most convenient for timing, the number of drops per second equivalent to any given number of c.c. per minute may be readily ascertained with the condenser used. With a vertical condenser, having an end cut off square, one drop per second is usually approximately 4 c.c. per minute.

[2] In the process of shaking with concentrated sulphuric acid, small quantities of aromatic hydrocarbons are absorbed in addition to olefines, so that the percentages of the former subsequently found are always rather lower than the quantity present in the original material. As, however, in practice, the products have also always to be washed with concentrated sulphuric acid, the results obtained for the percentages of aromatic hydrocarbons truly represent the maximum quantities of these which could be obtained, provided that the washing to which they are subjected on the small scale is not more severe than that which they receive in large scale practice to remove the unsaturated compounds. The quantity of acid given above, namely, 8 per cent. of 95 per cent. acid with 5 minutes' shaking, has been found to effect a satisfactory removal of the unsaturated compounds with all samples tried, and not to cause extensive absorption of aromatic hydrocarbons, and such absorption of these as does take place chiefly affects the xylenes which are more readily attacked by sulphuric acid than is toluene, whilst benzene is still less affected.

Satisfactory washing can be obtained with many samples by the use of less than 8 per cent. of sulphuric acid, but it is not an easy matter to judge, except by trial, how far this can be reduced, and the use of the full 8 per cent. does not appear to cause undue removal of the benzene, and toluene in any case, if shaking is not prolonged for more than the specified 5 minutes.

The strength of acid used should closely approximate to 95 per cent. H_2SO_4. Water is then carefully added down the side of the separating funnel so that it floats on the top of the acid layer, which thus becomes visible. With some oils the darkening on shaking with acid is so great that the boundary between the two layers can only be perceived with great difficulty until water is added in this manner. The acid layer is then run off, and the oil washed by allowing a thin stream of water to fall through it without shaking. After running off the water, the oil is shaken successively with 10 per cent. aqueous caustic soda, and finally with water, only gentle shaking being employed so as to avoid, as far as possible, the formation of emulsions.

The difference between the volume now remaining after complete separation of water and the volume remaining after washing with alkali gives an approximate indication of the volume of unsaturated hydrocarbons (chiefly olefines) which have been absorbed by the sulphuric acid.

In addition to the olefines, other unsaturated hydrocarbons are present (dienes, etc.) which are not absorbed by the sulphuric acid, but in its presence chiefly undergo polymerisation, yielding high-boiling hydrocarbons of unknown constitution boiling mainly from 300° to 400° C., which remain dissolved in the oil, the olefines also yielding polymerised hydrocarbons to some extent. The actual amount of such condensable hydrocarbons varies greatly, and is much higher in products derived from the carbonisation of petroleum products than in those obtained from coal. An approximate estimation of the quantity of these is obtained from the volume of the residue left at 200° on refractionating the washed oil.

This oil, after freeing from water as completely as possible, is again distilled from a round-bottomed flask fitted with a Young 12-bulb pear column, at the rate of 4 c.c. per minute, and separated into fractions. The method of collecting the fractions is varied somewhat according to the composition of the washed oil.

(1) Where not less than 50 per cent. of the washed oil distils under these conditions below 90° C., the fractions are directly collected as follows :—

(*a*) up to 90°, this fraction then containing only benzene and toluene, together with carbon bisulphide, and paraffins of similar boiling-point.

(*b*) 90°–140°, this fraction consisting of benzene, toluene, and xylene, except for paraffins of similar boiling-point.

(*c*) 140°–160°, consisting of xylenes, cumenes, etc., with paraffins.

(*d*) 160°–200°, consisting of higher homologues of benzene, with some paraffins.

(*e*) Residue at 200°, consisting chiefly of the polymerised hydrocarbons formed by the action of sulphuric acid on the dienes, etc., in the original tar or oil.

(2) If the amount boiling below 90° is less than 50 per cent., as is often the case with crude naphtha from coal tar, some xylene may also distil over with benzene and toluene below 90°. Where the distillate up to 90° does not amount to 50 per cent., therefore, the first fraction is collected up to 95°, and the second fraction from 95°

to 140°, and the remainder of the fractionation made as in (1). The fraction up to 95° is then refractionated, and the distillate up to 90° collected. The residue at 90° contains all the xylene and is then added to the fraction 95°–140°, the combined amounts forming the fraction 90°–140°.

(3) When the proportion of xylene and higher-boiling constituents is low, it is often not possible to continue the distillation up to 140°, owing to vapours in the later stage all condensing in the fractionating column. In such cases, xylene is added to the residue after the fraction up to 90° has been collected, and the distillation then continued to 140°. In that case the determination of the fractions 140°–160° and 160°–200°, and residue at 200° is omitted, or if required, a larger quantity of the original oil must be taken. The xylene must not be added before the fraction up to 90° is collected, as otherwise xylene would come over with that fraction and would count in the analysis as toluene.

Sometimes the oil after washing with sulphuric acid, caustic soda, and then with water, forms a very persistent emulsion with the latter, which is only separated with great difficulty. In such cases, the emulsion may be steam distilled, when the polymerised unsaturated hydrocarbons remain behind, the distillation being continued until the volume of condensed water approximately equals half the volume of spirit condensed. The difference between the volume of the steam distillate obtained after separation of water and the volume of oil after acid washing, gives an approximate figure of the total unsaturated hydrocarbons present, *i.e.*, the combined amount of olefines and polymerised hydrocarbons. In the subsequent fractionation of the steam-distilled oil, this is stopped at 160°, and the residue at 160° taken as the fraction 160°–200°. Some loss of the lower-boiling constituents, especially of benzene, is, however, difficult to avoid when steam distillation is carried out.

Determination of benzene, toluene, and xylene in the fractions "up to 90°," "90°–140°," and in commercial benzole and commercial toluole

Before these methods can be adopted it is necessary that the samples shall be freed as completely as possible from unsaturated hydrocarbons and phenols. This is the case when the fractions have been properly washed with sulphuric acid and caustic soda as described, but in the case of commercial benzole and toluole this may not be the case.

The ordinary method of ascertaining whether such products are sufficiently free from unsaturated hydrocarbons consists in shaking 90 c.c. of the sample with 10 c.c. of sulphuric acid of 90 per cent. strength, and judging from the coloration of the acid layer whether these have been sufficiently washed, this not being the case if the coloration exceeds a deep yellow or light brown colour. This test, although useful as a quick test for works control purposes, is far from satisfactory as a reasonably accurate method for giving a comparative indication of the amount of unsaturated compounds present, and is by no means certain in its indications, some samples which are in reality well washed giving a bad discoloration, whilst others, in reality badly washed, may only give a slight discoloration. A much more satisfactory test, which is quickly carried out and gives a relative quantitative indication of the proportion of unsaturated hydrocarbons present, is the determination of the quantity of oxygen the sample will absorb from an acid solution of potassium permanganate, at the ordinary temperature. This test is carried out as follows :—

80 c.c. of water and 10 c.c. of dilute sulphuric acid (made by adding 1 part by weight of concentrated sulphuric acid to 3 parts by weight of water) are placed in a stoppered bottle of about 300 c.c. capacity, 10 c.c. of the commercial spirit to be examined added, and the whole shaken. The temperature of the liquid should be between 15° and 20° C.; 50 c.c. of $N/10$ potassium permanganate is then added, and the whole shaken continuously for exactly 3 minutes ; if at the end of the first half minute the permanganate solution is markedly decolorised, a further 50 c.c. of $N/10$ permanganate is added, and the shaking then continued for a further $2\frac{1}{2}$ minutes. The excess of permanganate is then destroyed by the addition of 10 c.c. of a 10 per cent. potassium iodide solution, with vigorous shaking. The resulting solution containing iodide is then titrated with $N/10$ sodium thiosulphate solution, shaking well between each addition, until both layers in the bottle become colourless. The end-point of the titration is sharply indicated by the final disappearance of the violet colour from the spirit layer, and there is no need to add starch as indicator unless the original spirit was coloured. The number of c.c. of thiosulphate solution required for the titration is deducted from the volume of permanganate solution taken, the difference given the number of c.c. of decinormal permanganate solution reduced by 10 c.c. of the sample under the above conditions, and this figure gives a comparative indication of the extent to which the sample contains oxidisable impurities. If the number of c.c. of permanganate solution reduced by 10 c.c. of the sample is multiplied by 0·008 (1 c.c. $N/10$ $KMnO_4$=0·0008 gram oxygen) the resulting figure gives the number of grams of oxygen absorbed from permanganate by 100 c.c. of the spirit.

Well-washed samples show the reduction of from 1 to 10 c.c. of permanganate for 10 c.c., or 0·008 to 0·08 gram oxygen absorbed per 100 c.c., but others give much higher figures owing to insufficient washing.

A completely unwashed spirit may also be tested in a similar manner to ascertain approximately the amount of washing it requires. In such cases, 10 c.c. of the sample is diluted with pure, well-washed benzene to 100 c.c., and 10 c.c. of the diluted spirit taken for the test.

Any insufficiently washed commercial benzole or toluole, *i.e.*, any sample giving a higher oxygen absorption than 0·2 gram per 100 c.c., should be subjected to further acid-washing before testing. For this purpose a volume of 150–250 c.c. of the sample is shaken with 2 per cent. of 95 per cent. sulphuric acid, if the oxygen absorption is about 0·2 gram per 100 c.c., an additional 1 per cent. of sulphuric acid being used for each additional 0·1 gram of oxygen absorption. After removal of the acid layer and washing with water, aqueous caustic soda and again with water as described on page 440, the washed spirit is transferred to a round-bottomed flask, fitted with a glass tube for the introduction of steam, and connected to a condenser, and distilled without introduction of steam until about two-thirds has distilled over ; steam is then carefully blown through the liquid until about 50 c.c. of water has condensed for each 100 c.c. of the sample taken. The difference between the volume of spirit in the distillate, and the volume originally taken, gives the loss due to acid-washing, the percentage of which is calculated and allowed for in determining the percentages of aromatic hydrocarbons in the original insufficiently washed sample.

Analysis of Fractions " up to 90° " and " 90°–140° "

The percentage of benzene and toluene in the fraction up to 90°, and of benzene, toluene, and xylene in the fraction 90°–140°, may be determined with considerable accuracy by distilling these under specified conditions from a simple distillation flask of standard dimensions, and a comparison of the volume of the fractions obtained between fixed temperature limits with those obtained by distilling mixtures of known volumes of the pure hydrocarbons in the same apparatus and under the same conditions.

The apparatus required for the purpose consists of: (1) A standard Engler 100 c.c. distillation flask, as employed in the petroleum industry, having the following dimensions: Internal diameter of bulb, 6·5 cm.: length of neck, 15·0 cm.: internal diameter of neck, 1·6 cm.; vertical height of side tube above surface of liquid when flask is charged with 100 c.c., 9·0 cm.; angle of side tube, 75·0°. Flasks which do not vary more than 3 per cent. from any of these dimensions may be employed.

(2) An efficient water-cooled condenser. This is preferably a 10-inch Liebig condenser placed vertically, the connection with the flask being made by an adapter, or by having the side tube of the flask sufficiently long and bending it to fit the upper end of the condenser. The condenser used must in any case be of a form which drains quickly and as completely as possible.

(3) A set of calibrated graduated cylinders (50 and 100 c.c.).

(4) An accurate thermometer, which is fixed in the distillation flask with the top of the bulb just below the bottom of the side tube. With the above dimensions of the flask, the length of stem below the cork is then about 100 mm.

The accuracy of the determinations probably depends more on the correct reading of the thermometer than on any other single point. The thermometer used should preferably have a bulb of moderate size and should be graduated in one-fifth degrees C. over a range of at least 70° to 130°; the 80° graduation mark should be about 140 mm. from the bottom of the bulb, so that when the thermometer is fixed in the flask in the correct position this point is well above the top of the cork.

Calibration of the thermometer.—The thermometer should be graduated with an immersion of 100 mm. (this being the extent to which the stem is heated by the vapours under the conditions of the test) and then no correction is necessary for the length of the mercury column not heated by the vapour. Previous to use, it should be verified, or the corrections ascertained, for the temperatures 80°, 85°, 90°, 100°, 105°, and 116°, with 100 mm. immersion. In order to avoid mistakes in reading the thermometer it is convenient to put a distinctive mark on it at the actual graduation found to correspond on that thermometer to the corrected temperatures 80°, 85°, 90°, 100°, 105°, and 116° Nat. Phys. Lab. standard.

Correction for barometer.—Before making a test, the reading of the barometer in millimetres (corrected to 0° C.) is taken, and the barometer correction ascertained from the usual formula, barom. corrn. $=0{\cdot}00012\,(760-p)\,(253+t^\circ)$, where $p=$ the height of the barometer in mm. corrected to 0° C., and t° the boiling-point. The magnitude of the correction increases with increasing boiling-point, but within the range 80° to 120° the following table of corrections for barometric pressures from 772 to 720 mm. is of sufficient accuracy :—

p	corr.	p	corr.	p	corr.
772	−0·55	754	+0·30	736	+1·10
770	−0·45	752	+0·35	734	+1·15
768	−0·35	750	+0·45	732	+1·25
766	−0·30	748	+0·55	730	+1·35
764	−0·20	746	+0·65	728	+1·45
762	−0·10	744	+0·75	726	+1·50
760	0·00	742	+0·85	724	+1·60
758	+0·10	740	+0·90	722	+1·70
756	+0·20	738	+1·00	720	+1·80

A thermometer which has been calibrated with the stem completely immersed may also be used for the test, but in that case the correction for unheated mercury column must be made in addition to the barometer correction, in accordance with the usual formula, stem correction $= 0{\cdot}000143\,(T-t^\circ)N$, where $T =$ the observed boiling-point, t° the temperature of the air around the unheated portion of the steam, and N the length of the emergent mercury column, expressed in scale degrees. Tables for the value of thi correction are given in Young's *Fractional Distillation* (Macmillan and Co.), page 13, and a graph for the purpose by Wheeler (*J.S.C.I.*, 1916, 1198).

Before using a thermometer for the test, a few blank tests should be made with it, using mixtures made up of known amounts of pure benzene and toluene, and of pure benzene, toluene, and xylene, in order to ascertain that the results obtained with the thermometer are substantially correct. It has been found in one or two cases that certain thermometers, although quite correctly graduated, do not give correct results, as they have a pronounced lag. The cause of this has not been definitely ascertained, but appears to be due to the nature of the glass used in the manufacture of the thermometer. It is also advisable to carry out periodically similar blank tests on known mixtures with any thermometer in use for the analysis, to make sure that the readings given have not undergone change since its verification.

Method of distillation.—In carrying on the distillation, a measured volume of the liquid to be tested is distilled from the Engler flask at the rate of about 7 c.c. per minute. A slightly higher rate has no material effect on the results, but if the rate falls much below 7 c.c. appreciably increased fractional condensation takes place in the top and neck of the distilling flask, and may cause incorrect results. The flask is heated by means of a small Bunsen flame impinging directly on the bottom of the flask, the distillation being carried out at a spot as free from draught as practicable, a cylinder of fine wire gauze being also placed to surround the burner and flask up to the level of the top of the bulb of the flask. The distillates are collected in the graduated cylinders, and when the thermometer reaches the specified temperature, the flame is extinguished, the condenser allowed to drain, and the volume of the distillate measured.

Measurement of volumes and determination of specific gravity.—The specific gravities employed in the determinations are, throughout, those of the liquids at 15·5 C. compared with water at 15·5 C., and all volumes given are those of the liquids at 15·5° C. To correct the observed specific gravity at any other temperature to that at 15·5°, in the case of spirits, 0·0009 is added for each 1° C. the observed temperature is above 15·5°, or deducted for each 1° below that temperature. In the case of tar or products consisting chiefly of high-boiling oils, the factor used is 0·0007.

Fraction " up to 90° " and commercial benzole

When mixtures of benzene and toluene are distilled from a distillation flask under the specified conditions, the percentage of distillate at any given temperature is constant, and if the volume of distillate from 100 c.c. of the mixture to any temperature is determined for a definite rate and for a definite size of fractionating flask, then with an unknown mixture of benzene and toluene the percentages of benzene and toluene can be found by comparing the volume of distillate obtained under the same conditions with that found in the case of mixtures containing known amounts of the two constituents (James, *J.S.C.I.*, 1916, 236).

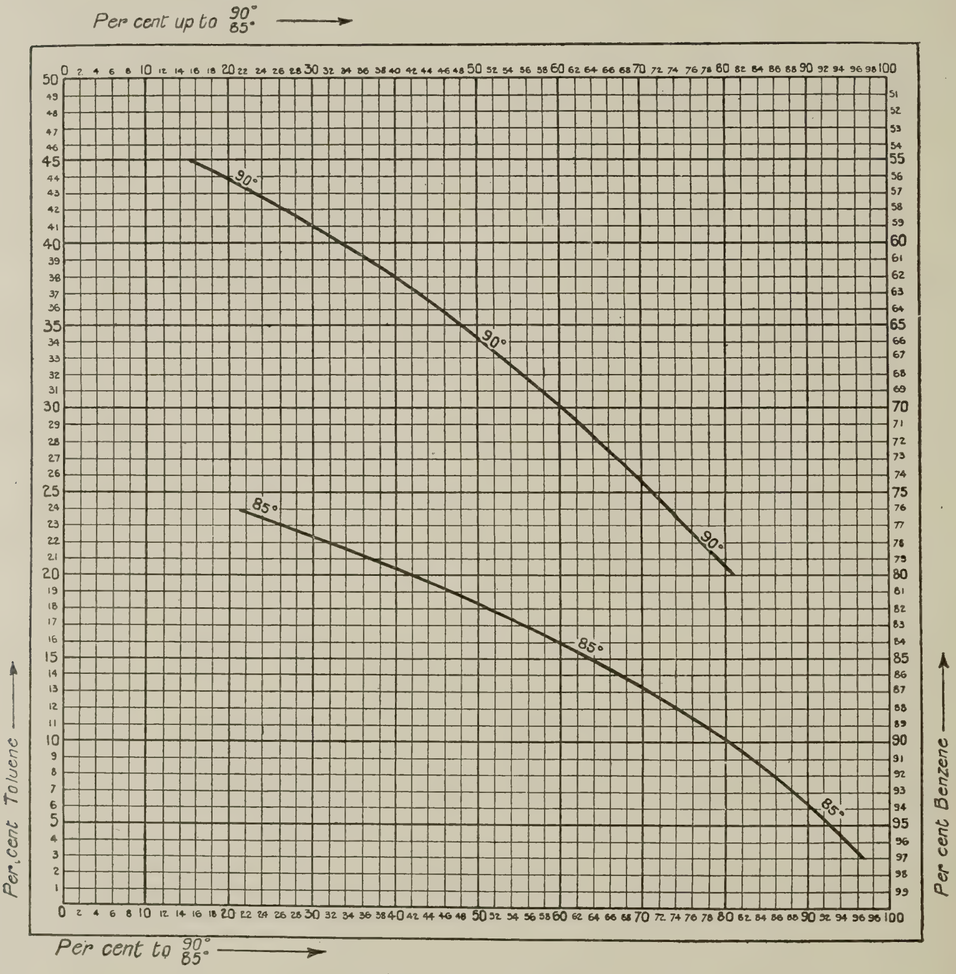
The results obtained with pure mixtures of benzene and toluene are most conveniently plotted out in the form of a graph, temperatures suitable for the collection of the distillate being 85° corr. for mixtures containing up to 25 per cent. of toluene, and 90° corr. for mixtures containing from 20 to 40 per cent. of toluene. The percentages of toluene are plotted as ordinates, and the percentages of distillate as abscissæ. In compiling Graph 1 the following mixtures were employed :—

Up to 85° corr.		Up to 90° corr.	
Benzene. c c.	Toluene. c c.	Benzene c c.	Toluene. c.c.
97	3	80	20
94	6	75	25
90	10	70	30
85	15	65	35
80	20	60	40
75	25	55	45

In the case of the fraction "up to 90°" or of any mixtures of benzene and toluene only, not containing more than 45 per cent. of the latter, 100 c.c. (or less if the quantity available is insufficient) is distilled from the Engler flask under the same conditions and the percentage of distillate to 85° corr. or 90° corr. ascertained. From Graph 1 the percentage of toluene is read off corresponding to the percentage of distillate found, that of benzene being found by difference.

Carbon bisulphide and paraffins.—When these impurities are absent, the reading obtained from the graph gives directly the percentages of benzene and toluene in the sample. The percentages of the above impurities, when present, can be ascertained together with the necessary correction in the amounts of benzene and toluene, from a determination of the specific gravity of the fraction or sample before and after removal of carbon bisulphide from it.

Carbon bisulphide.—To carry out this determination, the specific gravity of the sample is taken by any method giving results accurate to the third place of decimals.



BENZENE-TOLUENE GRAPH 1.

A further 100 c.c. (or the combined distillate to 85° or 90° and the residue from the distillation test) is then mixed with 100 c.c. of alcohol or industrial methylated spirit (free from paraffins), 5 grams of roughly powdered caustic soda added, and the whole shaken for five minutes; 200 c.c. of water is then added, with renewed shaking; after settling, the lower aqueous layer is run off, and the spirit washed twice with successive quantities of 25 c.c. of water and dried with ignited calcium chloride. The specific gravity of the dried spirit is then taken accurately to the third decimal place.

From the specific gravity of the spirit before and after removal of carbon bisulphide, the percentage of carbon bisulphide present may be calculated (see Nickels, Allen's *Comm. Org. Analysis*, Vol. II., part 2, page 183; Spielmann, *J.S.C.I.*, 1916, 396) on the assumption that the specific gravity of carbon bisulphide is 1·27 and that no expansion or contraction occurs on mixing the latter with benzene or mixtures of benzene and toluene, for then if a is specific gravity of spirit after removal and b the specific gravity before removal of CS_2, and x the percentage by volume of CS_2, $1{\cdot}27x+(100-x)a=100b$, or $x=100\times(b-a)\div(1{\cdot}27-a)$.

In fact, however, the assumption that no expansion or contraction occurs on mixing carbon bisulphide with benzene or mixtures of benzene and toluene is incorrect, as appreciable expansion does occur (see F. D. Brown, *J. Chem. Soc.*, 1879, 35, 552; 1881, 39, 205), and the observed specific gravity of mixtures of benzene or of benzene + toluene with carbon bisulphide in known proportions is always lower than that calculated from the percentage of the components and their specific gravity by a definite amount, k, and to obtain the percentage of carbon bisulphide by volume corrected for this expansion the value, $b+k$, must be substituted for b in the above formula, which then becomes

$$x=100\times\left\{(b+k)-a\right\}\div(1{\cdot}27-a).$$

The value of k varies with different proportions of carbon bisulphide and also slightly with differences in the proportion of toluene present, but an average figure for this value for percentages of carbon bisulphide up to 5 per cent. may be taken without material error as follows:—

% CS_2	k
1	0·0010
2	0·0015
3	0·0020
4	0·0024
5	0·0027

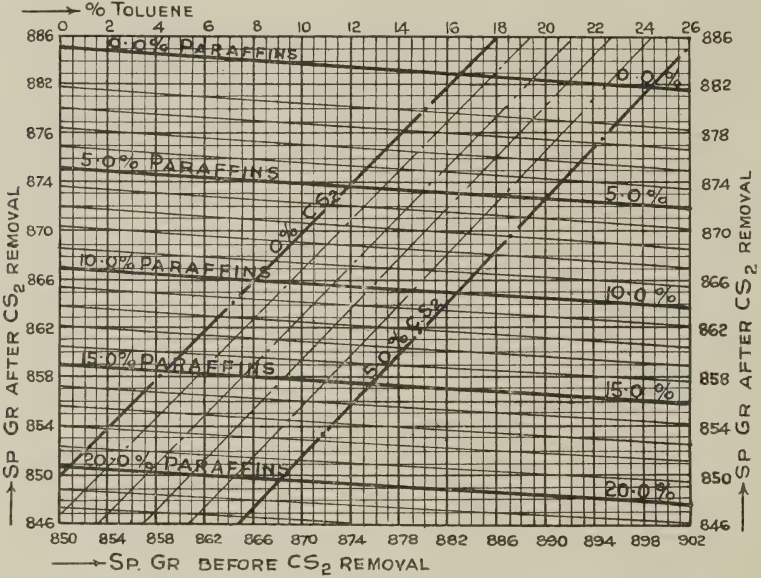
Graph 2 has been compiled to enable the direct reading off of the percentage of CS_2 in the sample from the specific gravity before and after removal of CS_2, the correction for expansion being made in setting out the graph. The lower line of ordinates gives the observed specific gravity before CS_2 removal, and the abscissæ the observed specific gravity after CS_2 removal, the percentage of CS_2 being read off from these on the broken black lines marked 0–5 per cent. of CS_2.

Paraffins.—In a similar manner, the percentage of paraffins present may be calculated from the observed specific gravity of the sample after removal of CS_2, and the specific gravity which a sample containing the percentage of toluene found would have if paraffins were absent. As no material expansion occurs on mixing benzene and toluene, at any rate with the amounts of the latter found in the fraction "up to 90°" or in commercial benzole, this last figure may be directly calculated with sufficient accuracy from the percentage of benzene and toluene found by the distillation to 85° or 90°.

Expansion does, however, occur on mixing paraffins with benzene or mixtures of benzene and toluene, and correction must be made on this account in the case of paraffins as well as with CS_2, and the necessary formula becomes :—
percentage by volume of paraffins in CS_2-free spirit

$$=100\times\{(a+k')-c\}\div(p-c).$$

where a is observed specific gravity after CS_2 removal, c the specific gravity of paraffin-free benzene-toluene mixture calculated from the distillation to 85°, p the specific gravity of paraffins, and k' the correction for expansion.



GRAPH 2.—PERCENTAGE OF CS_2 AND PARAFFINS IN FRACTION "UP TO 90°" AND IN COMMERCIAL BENZOLE.

The exact specific gravity of the paraffins present is unknown, but it has been found by isolation of them from these products that this may be taken without material error as 0·730 in this fraction up to 90° or in commercial benzole. The value of k' also varies considerably according to the percentage of paraffins present (the expansion being much greater on the addition of the first 1 per cent. than for any succeeding 1 per cent.) and also slightly with the percentage of toluene in the mixture, but for practical purposes the following values of k' may be taken.

Paraffins %	k'
1 . . .	0·0017
5 . . .	0·0021
10 . . .	0·0025
15 . . .	0·0029
20 . . .	0·0033

From the observed specific gravity of the sample after removal of CS_2 and the percentage of toluene found by Graph 1 uncorrected for paraffins, the percentage of paraffins in the sample after removal of CS_2 may be read directly from Graph 2. The upper line of ordinates gives the " uncorrected " percentage of toluene found, and the abscissæ the observed specific gravity of the sample freed from CS_2, the percentage of paraffins being read off from these on the full black lines marked 0–25 per cent. of paraffins.

The percentage of paraffins thus found, is that in the sample after removal of CS_2, and to obtain the true percentage of the paraffins in the original sample, this figure must be multiplied by 100–C, and divided by 100, where C is the percentage of CS_2 found in the sample.

The percentages of benzene and toluene found by Graph 1 are those which would be the case if no carbon bisulphide and paraffin were present. The total number of volumes of benzene+toluene present in 100 volumes is $100-C-P$, where C and P are the percentages found of these two impurities. In the distillation to 85° or 90°, carbon bisulphide behaves as though it were benzene, and if paraffins are absent but CS_2 present, the result obtained by Graph 1 gives the true percentage of toluene correctly, and the true benzene figure is $100-C-T$, where T is the percentage of toluene found.

Whether the paraffins, when present, are of such boiling-point that they are proportionately divided between the benzene and toluene fractions is uncertain and probably variable with different samples, but the evidence appears to show that they are in fact roughly proportional, and that if this is assumed no material error results.

Making this assumption when CS_2 and paraffins are present, the percentages of benzene and toluene may be calculated as follows : The total volume of benzene and toluene present is $100-C-P$. Then if B^1 and T^1 are the percentages of benzene and toluene found by Graph 1 from the percentage distilling to 85°, and B and T the true percentages of benzene and toluene corrected for paraffins and carbon bisulphide present,

$$B=(100-C-P)\,(B^1-C)\div(100-C),$$
$$T=(100-C-P)T^1\div(100-C).$$

With most products from tar consisting chiefly of benzene, the percentage of paraffins and CS_2 present is comparatively small, that of carbon bisulphide being mostly from 0·5–1·5 per cent., and that of paraffins not exceeding 5–6 per cent., being in the majority of cases much less ; in such samples the percentage of benzene and toluene corrected for these may be obtained with sufficient accuracy by a simpler calculation, namely by multiplying the percentages of those found by Graph 1 by 100 *minus* the combined percentages of carbon bisulphide and paraffins found by Graph 2, and dividing by 100, in which case

$$B=B^1\times(100-C-P)\div100, \text{ and}$$
$$T=T^1\times(100-C-P)\div100.$$

With only such amounts of carbon bisulphide and paraffins present, the figures obtained by the shorter method differ only by fractions of 1 per cent. from those found by the longer method, *i.e.*, by an amount which is smaller than the unavoidable experimental errors. The longer method is only necessary with products such as the "fore-runnings" collected in large-scale distillation previous to collecting "commercial" benzole containing much CS_2 (see Spielmann and Butler-Jones, *J.S.C.I.*, 1916, 911) and with products containing very high proportions of paraffins, such as are sometimes obtained from vertical retort tars, or from the low temperature carbonisation of coal.

Commercial benzole.—Samples of commercial benzole may be analysed by the method given for the "fraction up to 90°" (see page 445), but in certain cases slight modifications are advisable, namely, if (1) the percentage of toluene present is less than 3–4 per cent., and (2) if the percentage of toluene is high.

Where the percentage of toluene is below 3–4 per cent., the method is slightly modified by distilling to 85° a mixture of 95 c.c. of the sample with 5 c.c. of pure toluene. From Graph 1 the percentage of toluene in this mixture is read off from the percentage distilling to 85°, and this figure *minus* the 5 c.c. of toluene added, multiplied by 100 and divided by 95, gives the percentage of toluene in the original sample, the difference between this figure giving the percentage of benzene in the sample, if carbon bisulphide and paraffins are absent. The corrections for these are ascertained as specified above.

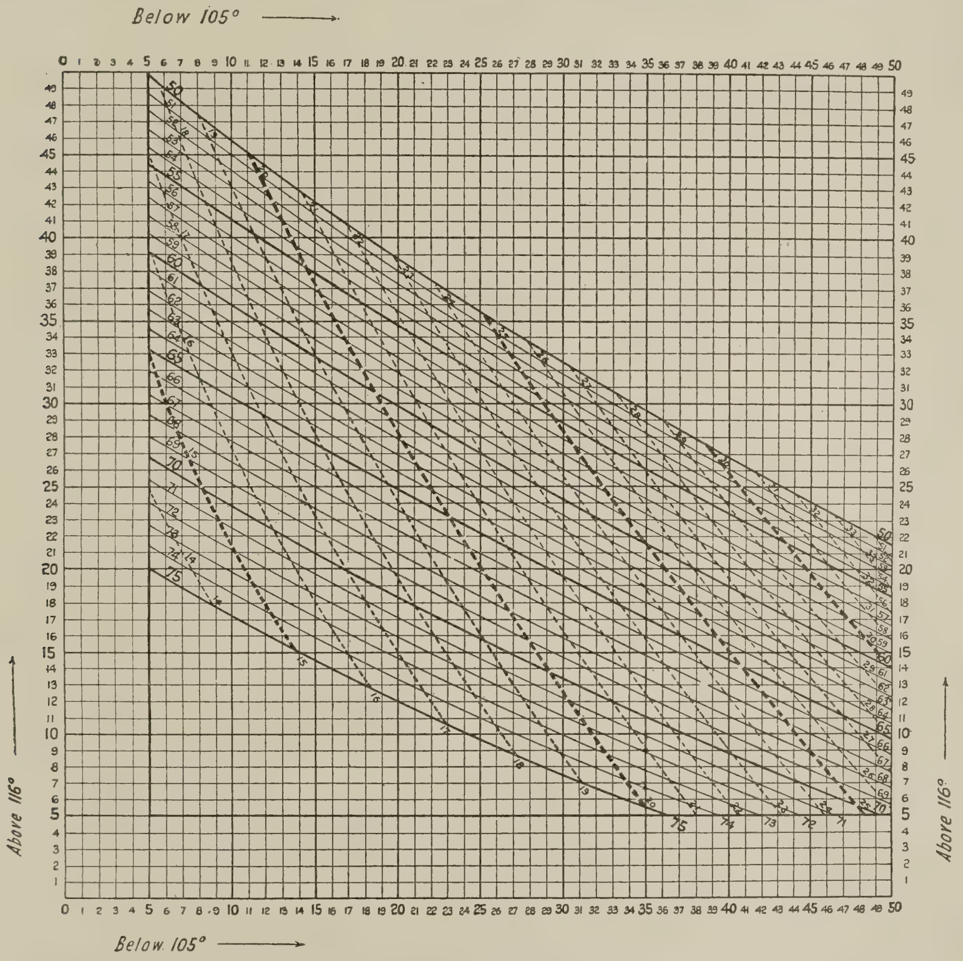
Where the percentage of toluene is high, this is mostly accompanied by small quantities of xylene, and in the test such xylene counts as an equal amount of toluene. For many purposes this is immaterial, and the results given by the test are correct if the figure found for toluene is recorded as "toluene+xylene." If it is desired to ascertain the separate percentages of toluene and xylene, 500 c.c. of the sample is distilled with a Young 12-bulb pear column, the fraction "up to 90°" analysed as above, and the residue at 90°, consisting of benzene, toluene, and xylene, analysed by the method given below for the "fraction 90°–140°." With a product such as the commercial 50/90's benzole, which always contains considerable amounts of xylene, this procedure is always advisable.

Unwashed benzole.—In some works it is the practice to fractionate the crude naphtha previous to washing with acid, etc., and then to subject the unwashed benzole and unwashed toluole separately to the washing process.

To analyse such a sample of unwashed benzole, it is washed with 8 per cent. of its volume of concentrated sulphuric acid, in the manner described on page 439. The washed spirit is transferred to a round-bottomed flask, fitted with a tube for introducing steam, and distilled with steam as already described (p. 438). The distillate after removal of water is analysed by the method just described, due allowance being made for the loss on acid washing in calculating the percentages of benzene, toluene, carbon bisulphide, and paraffins in the original unwashed sample.

Fraction 90°–140° *C. and commercial toluole*

The principle upon which the determination of the percentages of benzene, toluene, and xylene in such samples is carried out is as follows: When the distillation of mixtures of these hydrocarbons in known proportions is carried out in the same apparatus and under the same conditions as described for the "fraction up to 90°," it has been found that the percentage of the distillates obtained between fixed ranges of temperature is quite constant, and that if a graph be drawn up in which the percentages boiling below a fixed temperature are plotted as ordinates, and the percentages of residue at a higher fixed temperature as abscissæ, the points on the graph corresponding to the known percentages of benzene and toluene in the mixture lie on regular curves. From the results obtained in a large number of distillations of mixtures containing varying but known amounts of pure benzene, toluene, and xylene and measuring (1) the percentage boiling up to 105° corr. and (2) the residue left at 116° corr., Graph 3 has been plotted in the manner mentioned, the continuous line curves giving the percentage of toluene and the broken line curves the percentage of benzene



Benzene-Toluene-Xylene Graph 3.—Benzene Curves Black Dotted. Toluene Curves Black Full.

corresponding to the percentages of distillate up to 105° and above 116°. With a mixture of benzene, toluene, and xylene in unknown quantities, the percentages of distillate up to 105° corr. and above 116° corr. are ascertained and the percentages of benzene and toluene present may then be directly read off on Graph 3 from the broken line curves and full line curves respectively. The percentage of xylene is found by difference. There seems no reason why a similar method should not be employed for determining three successive members of any homologous series provided that they do not form constant boiling mixtures and that their boiling-points are not too close together.

NOTE.—In the method as originally published, the temperatures for the interruption of the distillation were taken as 105° and 117°, and for special reasons which were only of a temporary nature the thermometer graduated with complete immersion of the stem, and an approximate correction for barometer and unheated stem employed. For several reasons it has been found better to employ a thermometer graduated with 100-mm. immersion to avoid the necessity of making any correction for unheated stem, which makes slight alterations in the form of the graph, and in order to avoid confusion between the old and new graphs, the latter was drawn up for a different temperature interval.

The method, with the specified interruption points of 105° and 116° only holds generally for samples containing 50–75 per cent. of toluene, and for such as give at least 5 per cent. of distillate up to 105° and 5 per cent. above 116°. Samples which do not fall within these limits can, however, be readily analysed by the method by adding to them such known amounts of pure benzene, toluene, or xylene as bring the mixture within these limits, and distilling the mixture under the standard conditions. From the percentages of benzene, toluene, and xylene found in the mixture, and from the known amounts of benzene, toluene, or xylene added to it, the percentages of the hydrocarbons in the original sample are readily calculated.

If in addition to xylene small quantities of cumenes or similar higher boiling aromatic hydrocarbons are present, the results obtained by the test are unaffected, except in so far that the difference figure between 100 and the percentages of benzene plus toluene then gives the percentage of xylene plus higher boiling aromatic hydrocarbons instead of that of pure xylene.

Carbon bisulphide, if present in the sample in more than a small amount, renders the results less accurate, but it is never present in appreciable amount in the fraction 90°–140° prepared as described. Commercial products, such as 50/90's benzole, may contain more of this impurity, but such samples, as already mentioned, should first be distilled into a fraction up to 90° and residue at 90°, and the two fractions analysed separately.

Paraffins, when present, affect the results somewhat, but a correction for the error thus caused and an estimation of the percentage of paraffin present can be ascertained from the specific gravity of the sample in the manner described later.

Method of distillation.—As in the case of the fraction " up to 90°," 100 c.c. of the fraction 90°–140° is distilled from the standard Engler flask at the rate of about 7 c.c. per minute. When the thermometer shows a temperature of 105° corr. the distillation is stopped, the condenser allowed to drain, and a fresh cylinder placed under the condenser. The distillation is then continued under the same conditions until the thermometer shows a temperature of 116° corr., when the distillation is again interrupted. The residue, after cooling, is poured into a third cylinder, and the contents of the three cylinders are measured at a temperature approximating to that of the 100 c.c. taken for analysis. The total volume of the three fractions up to 105°, 105°–116°, and above 116°, should not amount to less than 99·5 c.c.

In the absence of paraffins, the percentages of benzene and toluene are directly read off from the percentages below 105° and above 116° by means of Graph 3.

If, as the result of the distillation, values for the fractions up to 105° and above 116° are obtained which give no value for benzene and toluene on Graph 3, owing to the composition of the sample being such that it does not fall within the limits already specified, a further portion of the sample is taken less than 100 c.c. and made up to 100 c.c. with a known amount of pure benzene, toluene, or xylene. The quantities of these which it is necessary to add vary according to the composition of the sample, but with a little practice it becomes very easy to estimate the amounts which should be added. The following are examples frequently met with :—

(1) The percentage of the sample boiling either up to 105° or above 116° may be below 5 per cent. In this case 90 c.c. of the sample is taken and mixed previous to distillation with 10 c.c. of benzene, if the distillate up to 105° was below 5 per cent., or with 10 c.c. of xylene if the residue above 116° was below 5 per cent. Thus if the first test showed less than 5 c.c. below 105°, and a mixture of 90 c.c. of the sample with 10 c.c. of benzene gave 10 c.c. to 105° and 21 c.c. above 116°, then from Graph 3 the amount of benzene in the mixture is 15 per cent., and that of toluene 72 per cent. As 10 c.c. of benzene was added, the 90 c.c. of the original sample contains 15—10= 5 c.c. of benzene and 72 c.c. of toluene, whence, in the original sample benzene= $5 \times 100 \div 90 = 5{\cdot}5$ per cent.; toluene$=72 \times 100 \div 90 = 80{\cdot}0$ per cent.; xylene$=100 - 5{\cdot}5 - 80 = 14{\cdot}5$ per cent.

(2) The percentage boiling both below 105° and above 116° may be below 5 per cent. In this case 80 c.c. of the sample may be mixed with 10 c.c. of benzene and 10 c.c. of xylene, or if the percentage of toluene is very high, 75 c.c. of the sample is mixed with 15 c.c. of benzene and 10 c.c. of xylene. The percentage of benzene found in the mixture, less the quantity of benzene added and that of toluene found (without deduction) multiplied by the number of c.c. of original spirit taken and divided by 100, then gives the percentages of benzene and toluene in the original, that of xylene being found by difference.

(3) The percentage boiling above 116° may be so high that no reading can be obtained on the graph. With this class, 80 c.c. is mixed with 20 c.c. of benzene and the mixture analysed, the percentages of benzene, toluene, and xylene in the original sample being calculated in a similar manner.

(4) The percentage boiling below 105° may be so high that no reading can be

obtained on the graph. In such cases, which include samples with rather high percentages of benzene, and in many cases the fraction " 90°–140° " obtained as specified above, 80 c.c. of the sample is mixed with 20 c.c. of toluene. Where the percentage of benzene is very high, the mixture of 80 c.c. with 20 c.c. of toluene may still contain below 50 per cent. of toluene. This rarely occurs with the fraction 90°–140° obtained as specified, but may happen with products such as 50/90's commercial benzoles. In such cases a smaller volume of the original and a larger amount of toluene may be taken, but the smaller the proportion of the original taken, the greater is the unavoidable experimental error in the results. Where results are desired as accurate as possible, and the quantity of the sample available permits of it, it is then better to distil 250 c.c. of the sample with a column into the fractions " up to 90°," and " above 90°," and to analyse these separately, the first by the method given above for the fraction " up to 90° " and the second by that for the fraction " 90–140°."

Paraffins in fraction 90°–140°.—The results obtained in the manner described give the percentages of benzene, toluene, and xylene, on the assumption that no paraffins are present. When these are present, they count in the test as aromatic hydrocarbons, and thus bring about an error in the results. From blank tests made with mixtures of the three aromatic hydrocarbons with paraffins, it has been found that when the percentage of paraffins does not exceed 5–7 per cent., no material error is caused by assuming that the result for each of the three aromatic hydrocarbons is affected in proportion to the total percentage of paraffins present, and that the true percentages of benzene, toluene, and xylene may be obtained by multiplying the " uncorrected " percentages found as above by 100 *minus* the percentage of paraffins present and dividing by 100.

The percentage of paraffins present may be found with a fair degree of accuracy, from the specific gravity of the sample, in a manner similar to that employed in the case of the benzene fraction. The specific gravity of a mixture of benzene, toluene, and xylene of the "uncorrected" percentages found can be calculated from the specific gravity of pure benzene, toluene, and xylene.

If there were no expansion or contraction occurring when benzene, toluene, and xylene are mixed, and also no expansion or contraction on the addition of paraffins to this mixture, then if a is the calculated specific gravity of paraffin-free mixture, b the observed specific gravity of the sample, and c the specific gravity of paraffins present, the percentage of paraffins present would be :—

$$100 \times (b-a) \div (c-a).$$

But, in fact, expansion occurs both when benzene, toluene, and xylene are mixed and also on addition of paraffins to these mixtures. If k^2 is the fall in specific gravity due to expansion on mixing benzene, toluene, and xylene, and k^3 the further fall on addition of paraffins to this mixture, then

$$\%\ \text{paraffins} = 100 \times \frac{\{[b+(k^2+k^3)]-a\}}{\{c-(a+k^2)\}}$$

The value of k^2 varies somewhat, but within the range of the proportions of benzene, toluene, and xylene usually present in the fraction 90°–140° or in commercial toluole, it may be taken as having a constant value of 0·0010. The value of k^2+k^3 for the combined fall in specific gravity on mixing benzene, toluene, xylene and paraffins has been found experimentally as an average value as follows :—

Paraffins %	k^2+k^3
1	0·0012
2	0·0014
5	0·0019
10	0·0022
15	0·0025
20	0·0030

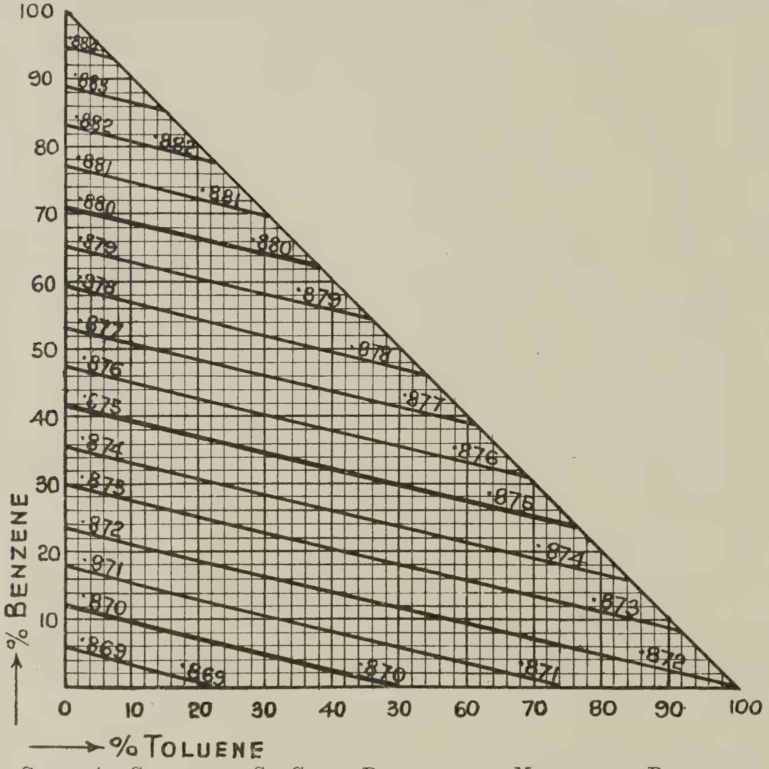
The average value of the specific gravity of the paraffins present in this fraction may also vary, but has been found by isolating them to be usually about 0·74 which is taken as the value of c.

The specific gravity of benzene, free from paraffin hydrocarbons, is 0·885. With regard to the specific gravity of pure toluene, authorities differ. The figure is usually given as 0·870, which is rarely exceeded in samples of commercial " pure toluene " obtained from coal tar. W. H. Perkin, senior, however (*J. Chem. Soc.*, 1896, 1191), showed that when such toluene is converted into the sulphuric acid and the latter purified and reconverted into toluene, the hydrocarbon thus obtained, absolutely free from paraffins, has the specific gravity of 0·8721, and a repetition of his work has confirmed this figure. The specific gravity of toluene, free from paraffins, is therefore taken as 0·872.

In the case of xylene, the specific gravity is in any case uncertain, as this is a mixture of *o*-, *m*-, and *p*-xylene, each of which has different boiling-point and different specific gravity. Perkin found the specific gravity of these three xylenes, when pure, to be : *o*-xylene 0·8818, *m*-xylene 0·8691, and *p*-xylene 0·8661 ; as the mixtures of xylenes from coal tar, etc., usually consist to the largest extent of *m*-xylene, with a smaller amount of *p*-xylene, and still smaller amounts of *o*-xylene, the average specific gravity of the xylene mixture entirely free from paraffins may be taken as 0·868. Commercial " pure xylene " rarely has a higher specific gravity than 0·865–0·866, and like the commercial " pure toluene," still contains small amounts of paraffins.

Having obtained the " uncorrected " percentage of benzene, toluene, and xylene in the sample in the manner already described, and also the specific gravity of the sample, the percentage of paraffins is determined as follows : From Graph 4 the calculated specific gravity of the mixture is read off from the percentages of benzene and toluene found (the specific gravity of the pure hydrocarbons being taken as 0·885, 0·872, and 0·868 respectively), and the percentage of paraffins is then read off from the observed and calculated specific gravities by means of Graph 5, which is drawn up from the formula given, allowing for the expansions which occur. The " corrected " amounts of benzene, toluene, and xylene are then obtained by multiplying the " uncorrected " figures by 100 *minus* the percentage of paraffins, and dividing by 100.

For many purposes it is frequently desired to ascertain the percentage present, not of the true paraffin-free toluene or xylene, but that of the percentages of ordinary "commercially pure toluene" of specific gravity 0·870 and of "commercially pure xylene" of specific gravity 0·865. To enable these percentages to be ascertained readily Graph 4A has been drawn up in exactly the same manner as 4, but taking the specific gravity of toluene as 0·870 and of xylene as 0·865, and the readings obtained from these Graphs 4A and 5 give directly the percentages of commercially pure toluene of specific gravity 0·870 and commercial xylene of specific gravity 0·865.



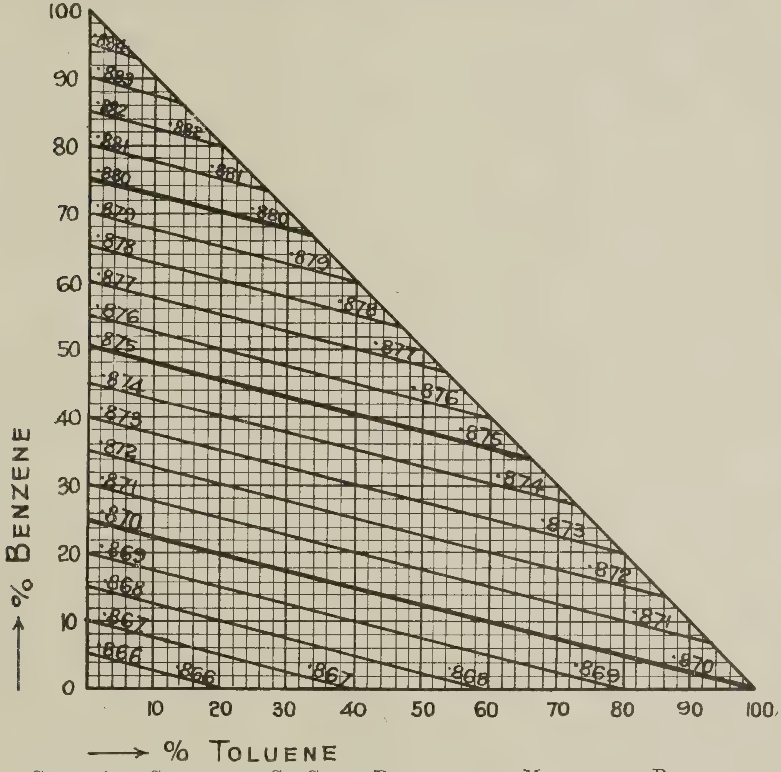
Graph 4.—Calculated Sp. Gr. of Paraffin-free Mixtures of Benzene, Toluene and Xylene.

Benzene = 0·885 Toluene = 0·872 Xylene = 0·868

The percentage of paraffins, of course, then comes out slightly less, as a small amount of these is included in the "commercially" pure toluene and xylene.

As previously stated when the percentage of paraffins exceeds about 7 per cent., the "uncorrected" figures obtained for benzene, toluene, and xylene are not necessarily in proportion to the true percentages present, and the "corrected" figures obtained in the manner specified may be in error to the extent of 2–3 per cent. With most coal-tar products, the percentage of paraffins rarely exceeds 5 per cent., but in certain samples, such as the products from coal tar obtained in vertical retorts, the percentage may rise to 20 per cent., and is often still higher with products obtained by very low-temperature carbonisation.

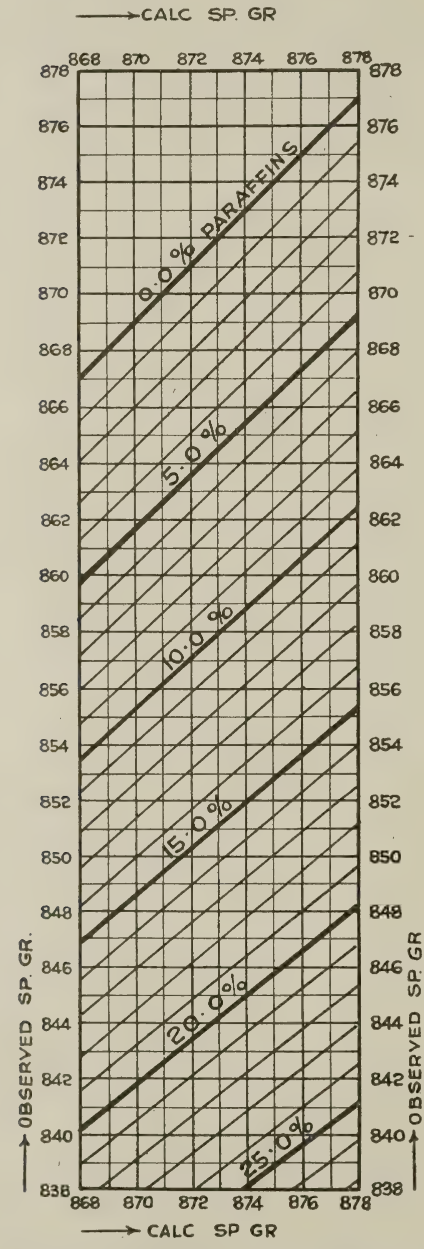
Blank tests with known mixtures of the aromatic hydrocarbons containing up to 10–25 per cent. of paraffins have shown that this error may be greatly reduced, if in the distillation of the fraction " 90°–140° " such quantities of benzene, toluene or xylene are added to it that the mixture contains between 52 and 58 per cent. of toluene uncorrected for paraffins, and on distillation gives not less than 20 per cent. respectively of distillate up to 105° and residue " above 116°." For percentages of paraffins above 25 per cent., whilst the method gives fairly accurate figures for the percentage of paraffins, no method has been found whereby it is possible to get accurate determinations of the percentages of benzene, toluene, and xylene present.



Graph 4a.—Calculated Sp. Gr. of Paraffin-free Mixtures of Benzene, Toluene and Xylene.

Benzene = 0·885 Toluene = 0·870 Xylene = 0·865

Unwashed toluole.—In some cases in works practice the toluole fraction is separated by distillation from the crude naphtha previous to acid washing. For the analysis of such samples, 150–250 c.c. of the spirit is washed with acid and steam-distilled in the manner described for unwashed benzole on page 438. If the percentage of xylene is not required, instead of steam-distilling the residual oil after treatment with sulphuric acid, etc., this may be distilled without steam, using a good column, and collecting the distillate to 140° (adding a little xylene if the thermometer does not reach 140°) and making up the distillate with pure xylene to the volume of unwashed toluole originally taken.



Graph 5.—Percentage of Paraffins in Fraction 90°–140° and in Commercial Toluole.

Fraction 140°–160°, *and commercial solvent naphtha*

The fraction 140°–160°, obtained from the preliminary distillation of coal tar, etc., in the manner described, consists of the constituents present in commercial coal-tar solvent naphtha, namely, xylenes, cumenes, and other aromatic hydrocarbons of boiling-points up to about 170° C. If to the percentage of this fraction found there is added the percentage of xylene (calculated on the original tar) found in the fraction 90°–140°, the combined figure gives an approximate estimation of the quantity of commercial solvent naphtha contained in the tar.

Owing to the large number of hydrocarbons present, and the fact that the boiling-points of the constituents are in many cases so near together, it is not possible by any distillation method to make any determination of the relative amounts of the individual constituents. The composition of the commercial products varies considerably, but when prepared from crude tar fairly free from paraffin hydrocarbons, its specific gravity is usually from 0·865 to 0·866. Each 0·001 that the specific gravity of a sample of xylene or solvent naphtha is found below 0·868 indicates the presence of approximately 1 per cent. of paraffins. The commercial product also often contains a higher percentage of unsaturated hydrocarbons than is the case with commercial benzole and toluole, since for many purposes for which solvent naphtha is employed the complete removal of these is unnecessary, and therefore the acid washing to which it is subjected in practice is less severe.

Benzene and toluene in commercial solvent naphtha.—The commercial product mostly contains varying amounts of toluene, and in addition sometimes contains small quantities of benzene. To determine with accuracy the amount of these hydrocarbons present, 250 c.c. of the sample is distilled with a good column at the rate of about 4 c.c. per minute, and the distillate to 142° collected. This first distillate is then again fractionated in the same apparatus, the distillate being now collected to 138° and its volume measured. This second distillate is essentially identical with a commercial toluole, rather high in xylene and low in benzene content, and is analysed by the method given above, the quantity of benzene and toluene found being calculated to percentages of the original solvent naphtha.

A quicker method, giving results sufficiently accurate for many purposes, is to distil 100 c.c. of the sample with a column, the distillate to 138° being collected in a 100 c.c. cylinder. To this is added 20 c.c. of benzene, and the contents of the cylinder then made up with toluene to 100 c.c. This mixture is then distilled, and the fractions " up to 105° " and above 116° determined, and the percentages of benzene and toluene in the mixture read off on Graph 3. The percentage of benzene found in the mixture less the 20 c.c. added, and the percentage of toluene found less the amount added to make up 100 c.c., give directly the percentages of benzene and toluene in the original solvent naphtha.

Fraction 160°–200°

The amount of this fraction, obtained from the original preliminary distillation of the tar or oil, gives an approximate figure of the amount of " heavy solvent naphtha " contained in the tar. Commercial heavy solvent naphtha, like the light solvent naphtha, consists chiefly of aromatic hydrocarbons, but in the heavy naphtha the boiling-point of these lies mainly from 160° to 200°. Any paraffins of similar boiling-point present in the original tar are also contained in this fraction. As with solvent naphtha, the number of constituents is so large and their boiling-points so close together, that their estimation by any distillation method is impracticable. The specific gravity of the fraction from different tars also varies so much that even an approximate estimation of the percentage of paraffins present is hardly practicable by this means.

Degree of accuracy of method

During the past four years some hundreds of blank tests have been made of mixtures made up with known amounts of pure benzene, toluene, xylene, carbon bisulphide, and paraffins in order to determine the degree of accuracy which may be expected in the analysis, especially of the fractions " up to 90° " and " 90°–140° " corresponding to commercial benzole and commercial toluole.

In the case of the fraction " up to 90°," when this consists of benzene and toluene only, the figures obtained show that when using an accurately calibrated thermometer and adhering to the conditions specified, the results given by the analysis differ only from the quantities actually taken by less than 0·5 per cent., and even when paraffins are present, unless their percentage is high, the results rarely differ from the true figures by more than that amount. The percentage of carbon bisulphide usually comes out correct within 0·1 per cent.

With the fraction 90°–140°, and in properly washed commercial toluole, in the absence of paraffins, the results obtained for all three constituents, benzene, toluene, and xylene, are almost always within 0·5 per cent. of the true figures. A series of 140 tests of mixtures of known amounts of pure benzene, toluene, and xylene in which the relative amounts were varied as much as possible, showed that of the 420 separate determinations of the three constituents, none differed from the correct figure by 1 per cent., and in only six cases was the error more than 0·5 per cent. The average quantities of benzene, toluene, and xylene in the 140 mixtures taken were as follows: Benzene 21·4 per cent., toluene 61·7 per cent., xylene 16·9 per cent., and the average quantities found were identical, the errors in the individual tests balancing each other.

With quantities of paraffins not much exceeding 5 per cent., the experimental error is slightly greater, but rarely exceeds 1 per cent. With higher percentages of paraffins the possible error increases, but if the precaution is taken mentioned on page 457 with regard to the composition of the actual mixture distilled to determine the percentages boiling below 105° and above 116°, the error rarely much exceeds 1 per cent. up to 25 per cent. of paraffins, though in the absence of this precaution the error in the percentage of toluene present may rise to 3 per cent. Above 25 per cent. of paraffins the magnitude of the possible error increases considerably.

The length of time required for the preliminary distillation of the tar or oil varies considerably according to the quantity of the latter which has to be taken to give a sufficient quantity of the light fraction for the further analysis, and also, as is well known, especially according to the amount of water and solid matter (" free carbon ") in the tar. The further complete analysis of the unwashed fraction to 200° takes from 3½ to 4 hours, but if the analysis of two or more samples is carried on simultaneously, the average time required is considerably less.

In the subjoined schedule, the detailed results are given resulting from the analysis of a " crude benzole " from gas made in vertical retorts, containing carbon bisulphide and a somewhat large percentage of paraffins, which exemplifies the carrying out of the method and the necessary calculations :—

Analysis of crude bensole from vertical retorts

Volume taken for analysis, 500 c.c., specific gravity at 15·5° C. 0·854 :—

Original sample

Distillate to 200°	462 c.c.
Residue at 200° (diff.) . . .	38 ,,

Unwashed fraction to 200°

Vol. after alkali washing . .	458 c.c.
Loss	4 ,,
Vol. after acid washing . . .	420 ,,
Loss	38 ,,

Fractionation of washed distillate

		Sp. gr.
Up to 90°	160 c.c.	0·856
90°–140°	147 ,,	0·840
140°–160°	37 ,,	0·824
160°–200°	30 ,,	0·840
Residue at 200° by diff.	46 ,,	—

Washed distillate "up to 90°"

100 c.c. gave 83·3 c.c. up to 85°.
From Graph 1. Benzene=90·0 % unc.
Toluene=10·0 % ,,
Sp. gr. before CS_2 removal, 0·856
,, after ,, 0·854
From Graph 2. CS_2=0·5% Paraffins=17·2 %

	% Comp. of fraction.	Comp. of 160 c.c.
CS_2	0·5 %	0·8 c.c.
Paraffins	17·2%	27·5 ,,
Benzene	74·1 %	118·6 ,,
Toluene	8·2 %	13·1 ,,

Washed distillate 90°–140°

81 c.c.+19 c.c. Toluene+0 c.c. Benzene.

		From Graph 3.
Up to 105°	39·8%	Benzene=29·3%
105°–116°	35·3%	Toluene =53·6%
Above 116°	24·5%	Xylene =17·1%

	In 81 c.c. of w.d. 90°–140°	In 100 c.c. of w.d. 90°–140°
Benzene, unc.	29·3	36·2
Toluene, unc.	34·6	42·7
Xylene, unc.	17·1	21·1

Sp. gr. of fraction . . . . . . 0·840
Calc. sp. gr. of paraffin-free sample from Graph 4 . 0·876
Therefore, from Graph 5 paraffins=24·7 %.

	% Comp. of fraction.	Comp. of 147 c.c. of fraction.
Paraffins	24·7%	36·3 c.c.
Benzene	27·2%	40·1 ,,
Toluene	32·2%	47·3 ,,
Xylene	15·9%	23·3 ,,

In order to check, as far as possible, the accuracy of the results, a mixture was made up of the number of c.c. found of CS_2, petrol (free from aromatic hydrocarbons) boiling from 80° to 140°, pure benzene, pure toluene, solvent naphtha free from toluene, and heavy naphtha. To the naphthas, however, were previously added paraffins of similar boiling-point to make their specific gravity approximately 0·83 and 0·84. This mixture was then analysed in the prescribed manner, the following results being obtained :—

	Taken %	Found %
CS_2	0·2	0·2
Paraffins to 140°. . .	17·1	16·5
Benzene	42·2	43·3
Toluene	16·2	16·5
Solvent naphtha . .	16·2	14·1
Heavy naphtha . . .	8·0	9·4

—	Fraction up to 90°.	Fraction 90°–140°.	Fraction 140°–160°.	Fraction 160°–200°.	Loss on alk. washing.	Loss on acid washing.	Fraction over 200° wash. dist.	Fraction over 200° original.	Total in 500 c.c. original.	Per cent. of original.
CS_2 . . .	0·8	—	—	—	—	—	—	—	0·8	0·2
Paraffins to 140° .	27·5	36·3	—	—	—	—	—	—	63·8	12·8
Benzene . .	118·6	40·1	—	—	—	—	—	—	158·7	31·7
Toluene . .	13·1	47·3	—	—	—	—	—	—	60·4	12·1
Solvent naphtha .	—	23·3	37·0	—	—	—	—	—	60·3	*12·0
Heavy naphtha .	—	—	—	30·0	—	—	—	—	30·0	*6·0
Loss on alk. wash	—	—	—	—	4·0	—	—	—	4·0	0·8
Loss on acid wash	—	—	—	—	—	38·0	—	—	38·0	7·6
Above 200° washed distillate . .	—	—	—	—	—	—	46·0	—	46·0	9·2
Above 200° in original .	—	—	—	—	—	—	—	38·0	38·0	7·6

* These contain approximately 40–45% paraffins.

Benzoles and Toluoles

In addition to Dr. H. G. Colman and Mr. E. W. Yeoman's paper dealing with methods of determination of benzene and toluene in coal-tar products, the reader is referred to the following papers by H. G. Evans on "The Estimation of Paraffins and Unsaturated Compounds in Commercial Toluols,"[1] "The Estimation of Paraffins in Commercial Toluol", by E. Lewis[2], "The Estimation of Paraffins in Commercial Toluol," by H. G. Colman,[3] and "Analysis of Commercially 'Pure' Benzene," by F. Butler Jones, B.A. (Cantab.), A.I.C.[4]

[1] *J.S.C.I.*, Vol. 38, No. 23, pp. 402T–405T.
[2] *J.S.C.I.*, Vol. 39, No. 4, p. 50T.
[3] *J.S.C.I.*, Vol. 39, No. 4, p. 50T.
[4] *J.S.C.I.*, Vol. 37, No. 24, pp. 324T–327T.

TESTING BENZOLISED AND DEBENZOLISED OIL FOR CRUDE BENZOLE CONTENT

Two hundred c.c. of the oil are placed in a retort with the thermometer in the liquid. The retort is connected to a moderately long air-cooled, or a short water-cooled, condensing tube and any distillate up to 160° C. collected in a 20 c.c. graduated measure. This distillate is considered as crude benzole.

A method of estimating benzoles in wash oils based on simply ascertaining the vapour pressure of the benzole dissolved was used at the Lyons Gas Works during the war, and is fully described and illustrated in the *Gas World.*[1]

According to the experience of Lance Shuttleworth, the most difficult and elusive of all tests connected with benzole plant efficiency are (1) the estimation of benzole in gas, and (2) the estimation of benzole in scrubbing oils. This worker gives a method of estimating benzole in gas and also in scrubbing oil in the *Gas World.*[2]

The determination of the benzole content of wash oil is dealt with somewhat fully in Whitehead's *Benzole,* and the reader is recommended to consult this work.

WASH OILS

A method of examining wash oils for removing benzole and naphthalene from gases by F. Pannertz[3] is as follows :—

Vessels containing 50 c.c. of crude benzole, 70 c.c. of the oil to be examined, 20 c.c. of dilute sulphuric acids, and 80 c.c. of, and 20 c.c. of, saturated picric acid solution are arranged in the order given, and 100 litres of pure air drawn successively through them. The absorbing capacity of the test oil for benzole is found by taking into consideration the loss in weight of the crude benzole, and the increase in weight of the test oil. An examination of the two picric acid vessels will clearly show whether the oil gives up too much naphthalene. Oils which act in this manner are, of course, quite unsuitable for use as scrubbing oils. In this process an advantage is obtained in regard to the estimation of naphthalene by picric acid ; it appears that traces of benzole vapour which are carried over render naphthalene picrate lighter, and instead of separating out it collects in layers of a flocculent nature in the upper part of the solution. If, further, a quantitative determination is required, a pipette with the top closed by pressing the finger on it can be pushed through the picrate precipitate, and the clear liquid sucked off. This method does away with filtering, which is liable to introduce error. Of course, it is necessary to weigh the picrate vessels before conducting the operation.

DETERMINATION OF BENZENOID HYDROCARBONS IN COAL GAS

Pending the discovery of something better, the following methods are given. They are said to yield satisfactory results if carefully carried out.[4]

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[1] *Gas World,* Coking Section, November 5th, 1921, p. 20.

[2] *Gas World,* Coking Section, July 2nd, 1921, p. 13.

[3] *Gas. u. Wasserfach,* 1922, 65, 113–115. See also *J.S.C.I.,* Vol. 15, 1922, p. 241A.

[4] See *Gas World,* Coking Section, August, 1916, p. 13.

To estimate benzole or toluole in coal gas by absorption is a rather difficult test, as at least 100 cubic feet of gas should be treated, the content of these oils being so low. But the oleic acid test for light oils in gas is, as a works test, fairly reliable, and useful where a stripping plant is in use. Three bubbling bottles should be used (about 1-inch seal in each bottle) containing the oleic acid (oleic acid B.P. is used) and a convenient amount of gas, say, 10 cubic feet, bubbled through. After this, the contents of the bottles should be steamed, *i.e.* steam bubbled through and condensed by passing through a suitable condenser, a measuring cylinder being provided to receive the condensate, which consists of water and light oil. The latter can be easily read off, say, as c.c. per cubic foot, and can be calculated to a convenient standard, say, gallons per ton of coal (4,543 c.c. to a gallon). Ten to fifteen minutes should be allowed for steaming. In that time all recoverable light oil will have come over; and, of course, after a series of tests, if the oil be retained, there would be a sufficient quantity of it to fractionate in the ordinary way, separating the water by means of a separator, and the last traces by means of the addition of a little calcium chloride. The oleic acid, after separation from water as the result of the steaming, may be used again, and will last some number of tests if a little fresh acid is added occasionally. This test is in use on several plants.

Müller's Method for the Determination of Benzole, etc., in Coal Gas[1]

Müller's method consists in passing a measured volume of gas first through a washing and drying train (consisting of two bottles containing 25 per cent. caustic potash solution, one bottle with 25 per cent. sulphuric acid, and two large tubes filled with granulated anhydrous calcium chloride), and then through four weighed absorption bottles of "oleum petroleum." These are connected to a fifth empty and weighed catch-bottle, followed by a drying tube and the gas meter. Interposed between the two last-named is a pressure gauge for correction of the results to N.T.P., if this is necessary. The five weighed bottles are placed in a shallow tray and surrounded by ice. The train is connected to the gas main before the benzole scrubber inlet, and gas is passed through at a speed of 10 litres per hour. The increase in weight of the five bottles is taken as the weight of benzole, etc., in the volume of gas washed. A similar train fixed to the gas main at the scrubber outlet will indicate what amount of benzole is left in the gas, and from the two figures the scrubbing efficiency is arrived at. The test should extend over at least twenty-four hours, and be timed to correspond with the times of emptying the "benzole daily production" tank, so that actual makes can be compared with the efficiency figures. The "oleum petroleum" of the British Pharmacopœia is used. Its specific gravity should be 0·88, its boiling-point 360° C., it should be non-volatile at ordinary temperatures, and should deposit no solids at 0° C.

Further particulars in regard to the determination of benzole in coal gas are given in Whitehead's *Benzole*,[2] to which the reader is referred.

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[1] See *Gas World*, Coking Section, February, 1917, p. 19.

[2] *Benzole, its Recovery, Rectification and Uses*, S. E. Whitehead. Benn Brothers, Ltd., London.

Wilson[1] and Bradley[2] favour the use of petroleum instead of oleic acid. The petroleum oil used must not yield anything under 200° C. when heated in a retort. Coal gas is passed through the petroleum, and the increase in weight of the petroleum after the passage of the gas is considered as benzenoid hydrocarbons, or else the petroleum is distilled after the gas has been passed through it and the distillate collected up to 120° C. (or 165° C.) is assumed to be crude benzole.

There is certainly a need for a rapid and reliable works test for benzenoid hydrocarbons in coal gas.

DETERMINATION OF NAPHTHALENE IN COAL GAS

Macleod and Henderson[3] recommend passing 0·7 cubic foot of gas per hour through a saturated solution of citric acid and then through a 10-bulb absorption tube containing 2·6 grams of recrystallised picric acid and about 100 c.c. of water. At the end of the test the contents of the absorption tube are washed into a 250 c.c. flask and heated to 40° C. (104° F.) on the water-bath until all the picric acid has dissolved. After cooling, the saturated picrate is filtered off and the unused acid titrated with $\frac{N}{10}$ soda. About 10 cubic feet of gas are passed through the apparatus, the actual amount being measured by the use of a meter.

C. J. Dickenson Gair[4] gives the following method: About 350 c.c. of acetic acid (sp. gr. 1·044) are taken in two Woulff's bottles or towers. A small Woulff's bottle containing 150 c.c. of picric acid solution is also placed after the acetic acid bottles to act as a catch, and a measured volume of gas, not more than 3 to 6 cubic feet usually, passed through at the rate of about 1 cubic foot per hour. If the gas is impure a bottle containing oxalic acid solution maintained at a temperature of 80° C. is fitted in front of the bottles containing the acetic acid. In the event of there not being sufficient pressure to force the gas through the wash bottles, or if the gas be under vacuum, use is made of a piece of apparatus which pulls the gas through the bottles by means of a water pump and then automatically separates it from the water, the gas passing through the experimental meter at the ordinary atmospheric pressure. After the experiment is finished, the acetic acid and picric acid from the bottles are mixed in a flask, and about 500 c.c. of concentrated picric acid solution added. Pure naphthalene picrate separates out at once, in large flocculent masses, which have the advantage of being extremely easy to filter. After filtering, the naphthalene picrate is dried *in vacuo* or in a warm room, and weighed.

To students and others who are interested in the determination of benzole in coal gas, the author would recommend that they studied a paper upon this subject by A. Thau, published in full in the *Chemical Age* of November 4th, 1922, pages 630 to 638.

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[1] *Gas World*, Coking Section, December 2nd, 1916, p. 11.

[2] *Gas World*, Coking Section, January 6th, 1917, p. 9.

[3] "Notes on Naphthalene in Coal Gas," *J.S.C.I.*, 1914, p. 299. Also *J.S.C.I.*, 1913, p. 76.

[4] *J.S.C.I.*, 1905, p. 1279.

Cresylic Acid

Specific Gravity.—This constant is determined either by a hydrometer or specific gravity bottle.

Water.—This material is usually estimated by distilling carefully 100 c.c. of the sample in an 8-oz. retort until all the water and 10 c.c. of oil have been collected in a measure. A little benzole is then added to the contents of the measure, with shaking, and the mixture allowed to stand in order to enable the water to separate, when a clear reading may be obtained.

Distillation.—This test should be conducted in a Wurtz or distillation flask connected to an air condenser. The percentage of distillate is read off, as a rule, at the following points : 194° C., 196° C., 198° C., 200° C., 202° C., and 204° C.

Naphthalene and Neutral Oils.—This is not an easy test to carry out, and at the best is only approximately accurate. Twenty grams of the sample are taken and placed in a separating funnel. The beaker in which the 20 grams were weighed is rinsed out with 100 c.c. of 15 per cent. caustic soda and the rinsings added to the cresylic acid in the funnel. The lot is well shaken, and when the acids have dissolved 100 c.c. of distilled water are added with thorough agitation. If a clear solution results, then naphthalene and neutral oils may be considered absent, but in the case of marked turbidity the mixture is extracted with light petroleum ether, which is dry at 75° C., the extract carefully separated, run into a weighed beaker or flask, the ether cautiously evaporated off on a water-bath and the residue weighed.

In cases in which the cresylic acid contains a fairly large quantity of oil and naphthalene, the following rough test may be used : Into a 100 c.c. stoppered test mixer 40 c.c. of 60° Tw. caustic soda are placed, and on the top of this 40 c.c. of cresylic are carefully poured. The two substances are thoroughly mixed and then allowed to cool down to 60° F., after which 5 c.c. of benzole are added and the lot shaken up. The contents of the test mixer are now allowed to stand in order that the benzole may separate, together with any oil and naphthalene which it has dissolved; the increase in volume of benzole may be taken as oil. The author does not altogether approve of this test.

Tar Acids in Cresylic.—If it is desired to estimate these, the following method may be used : 100 c.c. of the sample measured at 60° F. are placed into a separating funnel and about 100 c.c. of 60° Tw. caustic soda added to the same, and the lot well shaken until the cresylic has dissolved. The solution is then extracted with light petroleum ether, the ether extract carefully separated, and the cresylate of soda filtered through a little glass wool into a large beaker. It is brought up to the boil and kept at this point for about two minutes, after which it is allowed to cool down. It is then placed in a separating funnel, the beaker being rinsed out with a little water and the tar acids thrown up by the addition of dilute B.O.V. A sufficient length of time is given for the tar acid to separate properly, when the subnatant sulphate of soda liquor is separated, and the tar acids run into a measure and the volume read off.

Sulphuretted Hydrogen and Sulphur Compounds.—During the manufacture of cresol it is necessary to test it for sulphur compounds, and it is also advisable to examine samples which are being purchased for the same substances. The method generally used is to place about 50 c.c. of the cresol in a flask fitted with air inlet and outlet tubes, the inlet tube dipping into the cresol. The outlet tube is connected to another flask, which in its turn is fitted to a filter pump. In this flask a piece of lead acetate paper is suspended in such a position that it hangs over the air inlet tube. Air is aspirated through the cresol by means of the filter pump, and during its passage through the second flask it comes in contact with the acetate paper. Should sulphur compounds be present the paper will turn brown or black. A good sample of cresylic will not blacken an acetate paper after 15 minutes. Fig. 152 illustrates the arrangement of the flasks, etc.

Meta-Cresol—Cresylite Test

There is a special grade of cresylic acid manufactured which contains a considerable quantity of meta-cresol. This material is used for the manufacture of trinitro-meta-cresol. There are two methods of testing this substance, one of which is known as the short test and the other as the long test. They are carried out as follows :—

Short Test.—Ten grams of the cresol are placed in an Erlenmeyer flask and 15 c.c. of 60° Bé. sulphuric acid are added. The lot is well agitated, and then heated for one hour in a steam oven. After this the sulphonated mixture is poured into a 1-litre flask and thoroughly cooled under a water-tap. Into the Erlenmeyer flask in which the cresol was sulphonated 90 c.c. of 40° Bé. nitric acid are placed and thoroughly shaken until the sulphonated material adhering to the flask sides is rinsed off with the acid. It is then cooled a little and transferred rapidly to the contents of the litre flask. The lot is now vigorously shaken. In a few minutes reaction will take place. The mixture is now allowed to stand until the reaction is finished, when it is emptied into a large porcelain basin containing 40 c.c. of cold water. The flask is rinsed out with another 40 c.c. of cold water and the rinsings added to the contents of the basin, after which the lot is allowed to remain until the trinitro-meta-cresol crystallises out. It is then filtered through an ordinary filter paper, the crystals dried in a steam oven at 95 to 100° C., and weighed ; the result multiplied by 10 equals the cresylite test.

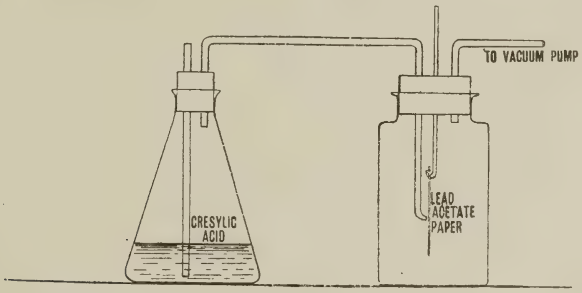

Fig. 152.—Apparatus used in Testing Cresylic Acid for Sulphur.

Long Test.—A retort of a capacity of 1 litre is fitted with a cylindrical dropping funnel, provided with a stop cock, holding about 50 c.c. The retort is placed in a spherical sand bath, about 14 cm. in diameter. The operation must be conducted in a fume cupboard. Into the retort 50 grams of nitric acid of 40° Bé. strength are placed and gently warmed to a temperature of 80° C. In the meantime 50 grams of the sample of cresol are mixed with 125 grams of sulphuric acid and allowed to stand for an hour. After this time has elapsed the contents of the flask are run into the dropping funnel and the flask inverted over it in order that it may thoroughly drain. The sulphonated cresol is allowed to drop into the nitric acid at such a rate that the whole of the contents of the dropping funnel will take between 1½ to 2 hours to run into the acid. The temperature must be kept at 80° C. the whole of the time and regular ebullition maintained. Red vapours are given off, and should these vapours whiten towards the finish, the test must be repeated with a larger quantity of nitric acid. The nitric acid should not be in great excess as the trinitro-meta-cresol is appreciably soluble in mother liquor charged with nitric acid. Immediately the whole of the sulphonated cresol has dropped into the nitric acid, the gas flame is removed and 20 minutes allowed to lapse, after which the contents of the retort are poured into a large porcelain basin containing 400 c.c. of cold water. The mixture is then left to cool for 24 hours, and the crystals which form are carefully separated from the mother liquor by decanting the latter into a filter funnel provided with a perforated filter disc and covered with round filter paper. The mass of crystals in the basin is melted in 200 c.c. of water, allowed to cool, the mother liquor removed as just mentioned, the crystals broken up, allowed to drain, dried at 50° C., weighed, and multiplied by two.

A communication by J. J. Fox and M. F. Barker,[1] entitled "Analysis and Composition of Cresylic Acid," deals with the methods whereby proportions of the three cresols in cresylic acid may be determined in a comparatively ready manner.

(There is a " Corrigenda " in the *J.S.C.I.* for October 31st, 1922, No. 20, page 338T, on the above paper.)

Some valuable work upon the solidifying and boiling-points of phenols and of cresols has been carried out by J. J. Fox and M. F. Barker and the results published in the *Journal of the Society of Chemical Industry.*[2]

CARBOLIC ACID

Specific Gravity.—This constant is determined by a hydrometer or specific gravity bottle.

Water.—This is generally determined during the carrying out of the crystallising test.

Solubility.—The sample is required to answer the following: 50 c.c. of the crude carbolic acid must be completely soluble in 100 c.c. of caustic soda of a specific gravity of 1·10.

Crystallising Point.—There are one or two methods of carrying this out, but that generally used for the buying and selling of crude carbolic acid is the following; and it is known in the trade as Lowe's method: Into an 8-oz. tubulated retort, having a neck about 15 inches long, 100 c.c. of the crude acid to be tested are placed.

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[1] *J.S.C.I.*, Vol. 39, No. 12, pp. 169T–172T.

[2] *J.S.C.I.*, 1918, pp. 268T–272T.

No condenser is connected to the beak of the retort, and the distillation is so regulated that no vapours are given off, and the operation occupies about two hours. Clean, dry, graduated cylinders must be used for the collection of the distillates. Into the first receiver 10 c.c. of oil and all the water (which latter shall not exceed 15 c.c.) are collected. The next $62\frac{1}{2}$ c.c. are collected in the second receiver, well mixed, and cooled slowly to near the expected crystallising point. A small quantity of pure crystals is then added, and the cooling continued—stirring all the time. When the distillate is crystalline throughout, the thermometer (a Fahrenheit graduated in one-tenths of a degree) is read ; and the figure indicated is taken as the crystallising point of the crude acid. It is often necessary to employ a cooling solution, and when this is the case care must be taken that the temperature of this solution is not more than 2° F. below that at which the sample is expected to crystallise.

With low crystallising acids—*e.g.* 50's and 45's, etc.—the determination of the point at which the first crystals appear is, unfortunately, rather a tedious process, and with the object of rendering it easier and quicker, the author and his assistant[1] made numerous experiments with a modified method, with very encouraging results. Up to the collection of the $62\frac{1}{2}$ c.c. of acid in the second receiver, the process is identical with Lowe's. The modification consists in just half-filling a test tube 5 inches long by $\frac{5}{8}$-inch in diameter with the well-mixed distillate, cooling while stirring until the contents of the tube are crystalline throughout—adding a small crystal of pure acid, if necessary—removing from the cooling mixture, and stirring slowly, at a temperature of about 60° F., until all crystals disappear. This point is called the liquefying point ; and if 2·5 is deducted from the figure obtained, the crystallising point of the acid is found. This figure was arrived at by taking the average of fifty experiments, the highest difference being 3·0 and the lowest 2·2.

A handy method for use in the works when making mixings is the following, and this method may be termed a short test : One hundred c.c. of the crude carbolic are distilled in an 8-oz. retort until all the water and 10 c.c. of the oil has come over. A further 20 c.c. of the tar acids are now collected in a perfectly dry cylinder, the crystallising point determined, as already explained under Lowe's test, and from the figure obtained 8 is deducted, when the result will indicate approximately the actual crystallising point. Another short test is the following : Into a 3-bulb Ladenburg flask of 150 c.c. capacity, 80 c.c. of crude carbolic are placed. The flask is connected to a 12-inch Liebig condenser, the jacket of which is filled with water, but no flow is maintained. All the water is distilled off, and 8 c.c. of the oil. Then into another perfectly dry receiver 50 c.c. of the tar acids are distilled and the crystallising point taken. If the figure 1 is deducted from the result, the crystallising point obtained by the long test is found approximately.

Tar Acids in Phenolate.—In order to control the working of the carbolic (and also the cresylic) plant, it is necessary to determine the amount of tar acids in the phenolate. This can be done rapidly by the following method : 100 c.c. of the phenolate are placed in a separating funnel and dilute B.O.V. (1 : 2) is added until the mixture is strongly acid to litmus paper. The lot is allowed to stand for a few minutes in order that the tar acids may separate completely, after which the sodium sulphate liquor is removed carefully and the volume of the tar acids measured.

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[1] "Investigations on Coal Tar and some of its Products." *English Junior Gas Associations' Joint Proceedings*, 1911–1912, Sec. M., pp. 105–125. *The Gas World*, March 2nd, 1912, p. 284.

ESTIMATION OF CARBOLIC ACID IN CRUDE PHENOLS

Mm. René Masse and Henri Leroux have presented to the French Academy of Sciences a note upon carbolic acid and the estimation of this in crude phenols from tar. The method still in use for the preparation of carbolic acid is that devised by Laurent in 1841, namely (1) Separation of phenols from creosote oils by shaking up with soda ; (2) acidification to set free the crude phenols, and (3) the extraction of the carbolic acid by rectifications and crystallisations. Good crude phenol, free from naphthalene, contains water, carbolic acid, orthocresol, metacresol, paracresol, xylenols, and homologues, and phenolic tarry matters. The chemical properties of carbolic acid and the cresols are so nearly related that there is no simple reagent which can separate them ; thus Koppeschaar's bromine method will not work if both orthocresol and metacresol be present. The physical properties, on the other hand, do enable us to discriminate. The boiling-points of phenol (carbolic acid), orthocresol, metacresol, and paracresol at 760 mm. barometric pressure are respectively 183°, 190·8°, 202·8°, and 201·8° C.; those of the xylenols are 220° and 225°. By fractionally distilling the crude phenol up to 203° C., and then fractionally distilling the fraction obtained between 180°–203° C. up to 198° C. (as described in the next paragraph), we can find the quantity of carbolic acid in each of these fractions by determining their respective crystallising points. Commercial carbolic acid, called 40° to 42°, has a melting or solidifying point slightly above 40° C.; commercially pure carbolic acid has a melting-point of 40·85° C. When we add cresols to pure carbolic acid the melting-point falls steadily, and that to very nearly the same extent whatever be the relative proportions of the three cresols, so long as the cresols added do not exceed 33 per cent. of the whole. The melting-point of the mixture thus depends on the percentage of carbolic acid, and the curve of melting-points is a straight line joining the two points phenol 100 per cent., melting-point 40·85° C. and 66 per cent., 21° C. This is the basis of the following working method :

Three kilograms of crude phenol are put in a still with copper vessel of 4 litres and a Vigreux column of 24 inches. The distillation is maintained at 7 to 8 c.c. per minute, and the following fractions are taken: (*a*) up to 180° (=water and phenols); (*b*) 180° to 203° ; (*c*) above 203°, 100 c.c. only. To (*a*) add enough chloride of sodium (35 per cent.) to precipitate the phenols contained in it ; decant these phenols and add them to (*b*). Put (*b*) into a flask of sufficient size ; wash out the vessels with liquid (*c*) and add this to (*b*). The liquid (*b*), with its additions, is now fractionally distilled at 4 c.c. per minute. The fractions taken are from 250 to 300 grams each, until the temperature of the vapours reaches 198° C. The solidification point of each fraction is then determined. A test-tube determination gives a rough indication; but with 30 to 40 grams, allowed to cool slowly until supercooled by 1° or 2°, the addition of a trace of crystallised carbolic acid determines crystallisation and the temperature goes up to the true melting-point. If in the test-tube trial the required temperature is below 21° C., add carbolic acid in known quantity sufficient to bring the percentage of carbolic acid above 66.

This method enables the carbolic acid in a crude phenol to be estimated with n 1 per cent., which is as near as could be expected with so complex a mixture as crude phenol.

In a paper entitled " The Determination of Phenols in Mixtures of Tar Acids," W. H. Hoffert[1] described a method which enables the phenol in any proportion in a mixture containing any or all of the three cresols to be directly determined, and the method depends on the fact that the lowering of the freezing-point of phenol hydrate by equal weights of each of the three cresols is the same.

H. M. Dawson and C. A. Mountford have published two long papers[2] dealing with the freezing-point of mixtures of phenol, *o*-cresol, *m*-cresol, and *p*-cresol, and the estimation of phenol and the three isomeric cresols in mixtures of these substances, the consulting of which will well repay the reader.

In regard to the estimation of phenol in cresylic acid, the reader is referred to the excellent papers published by J. J. Fox and M. F. Barker in the *Journal of the Society of Chemical Industry.*[3] The second paper by these authors has appended to it a bibliography of the most important literature dealing with phenol and cresol estimations and separations.

The student is recommended to study a paper entitled " Notes on Carbolic Acid ; Application of Phenol Tests to Works Practice," by George H. Sharples[4]. One section of this paper compares results obtained by the Weiss[5] method and Lowe's method. Another section deals with a method of determining small quantities of phenol in crude cresylic acid.

The reader is also referred to the following papers dealing with the determination of phenol in the presence of other phenols :—

" The Determination of Phenol in the presence of certain other Phenols," by A. M. Chapin, *J. Ind. Eng. Chem.*, 1920, 12, 771–775. This paper is abstracted in *J.S.C.I.*, October 15th, 1920, page 652A.

" The Determination of small quantities of Phenol in mixtures of Phenols," by F. Fischer and P. K. Breuer, *Ges. Abhandl. Kenntn. Kohle*, 1918, 3, 82–88. Abstracted in *J.S.C.I.*, April 15th, 1920, page 261A.

" The Estimation of Phenol in the presence of the three Cresols," by G. W. Knight, C. T. Lincoln, G. Formanek, and H. L. Follett. *J. Ind. Eng. Chem.*, 1918, 10, 9–18 ; abstracted in *J.S.C.I.*, February 28th, 1918, page 85A.

" The Determination of Phenol in Crude Carbolic Acid and Coal Tar Oils," by F. W. Skirrow, *J. Ind. Eng. Chem.*, 1917, 9, 1102–1106 ; abstracted in *J.S.C.I.*, February 15th, 1918, page 51A.

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[1] *J.S.C.I.*, October 31st, 1922, pp. 334T–337T.

[2] *J.C.S.*, 1918, No. 674, Trans., pp. 923–935, and pp. 935–944.

[3] *J.S.C.I.*, 1917, p. 842, and *J.S.C.I.*, 1918, pp. 265T–268T.

[4] *J.S.C.I.*, Vol. 37, No. 7, pp. 109T–113T.

[5] *J.S.C.I.*, 1913, p. 692.

ANTHRACENE TESTS

Crude and refined anthracenes are tested for the percentage of actual anthracene by what is known as Höchst test. The following materials are required: *Chromic acid solution.*—This is made by dissolving 150 grams of chromic acid (CrO_3) and 100 c.c. of glacial acetic acid in 100 c.c. of distilled water. *Fuming Sulphuric Acid Mixture.*—This is prepared by mixing equal parts of pure sulphuric acid of a specific gravity of 1·84 and Nordhausen sulphuric acid of a specific gravity of 1·92.

The test is carried out as follows: One gram of the sample is placed in a 500 c.c. boiling flask, and to it is added 45 c.c. of glacial acetic acid. The flask is connected to an air-cooled reflux condenser, and then placed on a sand-bath and the contents boiled until the anthracene is dissolved. In the meantime 35 c.c. of the chromic acid mixture are placed in a dropping funnel, the stem of which is inserted into the top of the reflux condenser. As soon as the anthracene is dissolved in the acetic acid, the chromic acid mixture is allowed to drop into the solution at such a rate that it will take two hours for the whole of it to run out of the dropping funnel. After all the chromic acid solution is in, the mixture is boiled for a further two hours and then allowed to stand for twelve hours. It is then diluted with 400 c.c. of cold distilled water and allowed to remain at rest for a further hour, after which it is filtered through a hardened filter paper and washed with (*a*) 200 c.c. of cold distilled water, (*b*) 200 c.c. of boiling dilute caustic potash solution (1: 1,000 water), and (*d*) 300 c.c. of boiling distilled water. The precipitate is now washed into a tared porcelain basin, dried on a water-bath, and finally in a steam oven at 100° C., and then weighed.

The weight obtained gives a figure which when multiplied by 85·6 is recorded as the common test.

To the material in the basin is now added 10 grams of the fuming sulphuric acid mixture, after which it is heated on a water-bath at 100° C., for 10 minutes. It is then stood in a damp place for 12 hours and then diluted with 200 c.c. of cold water, after which it is filtered through a hardened filter paper and washed with boiling water, soda, and boiling water, as before. The precipitate of quinone is then washed into a tared platinum dish, dried in a steam oven at 100° C., and weighed. After weighing, the basin and its contents are gently heated in order to volatilise the quinone, and when cold the basin and ash are reweighed. The difference between the first and the second weighings gives the weight of anthraquinone, and this multiplied by 85·58 will give the percentage of actual anthracene in the sample.

Material Insoluble in Benzole (*Sand, Dirt, etc.*).—Five grams of anthracene are transferred to a previously weighed extraction thimble, placed in a Soxhlet extraction apparatus and extracted with benzole in the usual way until the benzole leaves the apparatus colourless. The thimble is then removed, freed from benzole in a steam oven, cooled, and weighed. The increase in weight of the thimble indicates insoluble matter. It is necessary, of course, to cover the extraction thimble with a piece of filter paper, the edges of which may be bound with platinum wire, or else use a plug of cotton-wool.

Paraffin in Anthracene.—This may be estimated as follows: 10 grams of the sample are weighed into a large beaker and to it are added 108 c.c. of concentrated sulphuric acid. The mixture is heated on the water-bath until all the anthracene is dissolved, then it is cooled and poured into 400 c.c. of cold water contained in a 1,000 c.c. separating funnel. The mixture is allowed to cool and is then extracted twice with light petroleum ether (dry at 75° C.). The petroleum ether extracts are bulked and washed in a separating funnel, first with half its bulk of 5° Tw. caustic soda, and then four times with one-eighth of its bulk of cold concentrated sulphuric acid, and after this with cold water until free from acid. It is then allowed to settle, any water which separates removed, and then transferred to a tared flask, and the ether distilled off and the residue weighed.

H. F. Lewis[1] suggests a method for the separation of anthraquinone from anthracene and phenanthraquinone which consists in boiling a mixture with 5 per cent. sodium hydrozide solution and zinc dust, using an excess of these materials; the anthraquinone is reduced to oxanthranol and this substance goes into solution. After the reaction is over the mixture is filtered, and any insoluble portion submitted to further treatment with caustic soda and zinc dust. The total filtrate is shaken with air, when the oxanthranol is re-oxidised to anthraquinone, which is collected, dried and weighed.

DETERMINATION OF CARBAZOLE IN ANTHRACENE SALTS

The following process, a modification of the Kjeldahl method, is suggested by J. M. Clark,[2] and is said to give good results. A mixture of 0·5 gram of the material to be examined with 30 c.c. of strong sulphuric acid and 0·7 gram of mercuric oxide is digested for one hour over a low flame. The reaction mixture is then cooled, and, after the addition of 10 grams of potassium bi-sulphate, boiled until clear. The clear liquid is then cooled to 35° C., diluted with 200 c.c. of distilled water, and transferred to the usual distillation flask. Ten grams of sodium thiosulphate is now added, and when dissolved the mixture is made strongly alkaline and distilled. The distillate is collected and titrated in the usual way, and the amount of ammonia found calculated into carbazole.

NAPHTHALENE

Intermediate manufacturers now require commercially pure naphthalene to be almost chemically pure. It must be pure white, volatilise completely, melt between 79·3° and 79·8° C., and boil between 217° and 218° C. Phenols and quinoline bases must be absent. The former are tested for by boiling two grams with 30 c.c. of a 5 per cent. aqueous solution of caustic soda, cooling, filtering, and to the filtrate adding a few c.c. of bromine water and enough hydrochloric acid to produce an acid reaction. Any phenols present will be precipitated as bromo-phenols. Quinoline bases are found, if present, by dissolving about 5 grams of the naphthalene in concentrated sulphuric acid using the water-bath, cooling, pouring the solution into water, filtering off any separated naphthalene, making the filtrate alkaline and then submitting it to steam distillation, when quinoline bases will come over with the aqueous distillate and can be recognised by their smell. When dissolved in concentrated sulphuric acid and heated to 180° C. commercially pure naphthalene must not become dark in colour. If 15 grams of the naphthalene are dissolved in 6 grams of chemically pure sulphuric acid with gentle heat (water-bath) it should produce a clear solution of a pale pink colour, and if this solution is heated to 180° C., it should not change to more than a light brown in colour.

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[1] *Jour. Ind. Chem.*, 1918, 10, 425–426. See also *J.S.C.I.*, August 31st, 1918, p. 459A.

[2] *Jour. Ind. Eng. Chem.*, 1919, 11, 209.

EXAMINATION OF CAUSTIC LIQUORS, SPENT LIQUORS, AND LIME MUD IN CONNECTION WITH THE CO_2 PROCESS FOR MANUFACTURING TAR ACIDS

Spent Liquors.—It is essential that the causticised spent liquors be kept up to a standard strength as regards the percentage of actual caustic soda, and owing to the fact that impurities, sometimes to a moderately large extent, are always present in these liquors, it is not possible to control the strength with any degree of accuracy by the use of a hydrometer. It is necessary, therefore, to titrate the spent liquor with a standard acid solution for the amount of alkali present (calculated to sodium carbonate, Na_2CO_3), and then to add an amount of soda ash to the bulk of spent liquor in the causticisers to bring up the strength to the normal. The best results seem to be obtained by causticising spent liquor which contains 10 grams of Na_2CO_3 per 100 c.c. The author advises tarworks chemists who have control of a CO_2 plant for tar-acid recovery to work out a table for themselves, showing the amount of soda ash required for each causticiser as indicated from the results obtained from his analysis, allowing, of course, for the impurities in the soda ash used. For instance, assuming the spent liquor on analysis showed 9·8 grams of sodium carbonate per 100 c.c., then the material in the causticiser would require approximately 2·8 lbs. of soda ash (58 per cent. alkali) for every 100 gallons. The titration is carried out in the usual manner, but the liquor, as it is generally very dark, must be well diluted, and an indicator such as lacmoid or cochineal should be used.

Estimation of Caustic Soda in Lime Mud.—This may be rapidly estimated with a fair degree of accuracy by the following method: 20 grams of the mud are weighed in a 250 c.c. beaker and 100 c.c. of hot water poured on top of it. A gentle stream of carbonic acid is passed into the mixture for about 10 minutes, after which it is boiled, filtered, and the precipitate washed, the filtrate and washings being run into a 200 c.c. measuring flask. The contents of this flask are allowed to cool to 60° F. and then made up to 200 c.c. with distilled water and well mixed. An aliquot portion (say, 25 c.c.) is then removed by means of a pipette and titrated in the usual fashion, calculating to NaOH.

Estimation of Actual Caustic Soda in a Dark-coloured Causticised Spent Liquor.—As the causticised spent liquor is always very dark in colour, it is not possible to estimate the amount of caustic soda in the presence of carbonate by the method of double titration, which is used in the case of commercial caustic sodas. The following method gives very satisfactory results: 50 c.c. of the dark-coloured liquor (free from lime precipitate) are brought up to a temperature of 100° C. Barium chloride solution at a temperature of 95° to 100° C. is now added until no more precipitate forms. The lot is filtered while hot into a 250 c.c. measuring flask, the precipitate and filter paper washed with a little boiling water, and when cold the filtrate and washings are made up to the mark with distilled water, and an aliquot portion taken and titrated for caustic soda in the usual fashion.

TESTING THE COKE FURNACE GASES FOR USE IN THE CO_2 TAR ACID PROCESS

It is advisable that frequent tests of the gases be made as they leave the coke furnace, in order to control the efficient working of the CO_2 tar acid plant. The most convenient apparatus to use for this purpose is the Orsat. The manipulation of this apparatus is so simple that an intelligent works plant man may be taught how to use it satisfactorily in a very short time. It is advisable to estimate the carbon dioxide, oxygen, and carbon monoxide in each examination.

Coke.—The deliveries of this material should be examined for the amount of water, ash, and sulphur, and sampling before analysis must be carried out with care by one of the approved methods. To estimate the water, 20 grams of the ground coke are heated in an air oven to a temperature of 110° C. until of constant weight. The ash is determined by burning off 2 grams of the coke in a platinum dish and weighing the residue. Sulphur in coke may be estimated by Stock's method, which is as follows: 1 gram of coke in fine powder is mixed in a round-bottomed, platinum capsule with approximately 1 gram of half-hydrated caustic lime, moistened with water (1 c.c.), rapidly dried, and then heated in a muffle to bright redness until all carbon has disappeared. The mass is allowed to cool, transferred to a beaker, 20 c.c. of cold distilled water and 5 c.c. of bromine water added, and then $7\frac{1}{2}$ c.c. of pure strong HCl, after which the lot is boiled for 5 minutes. The contents of the beaker are then passed through a filter paper (filtrate must be bright), the beaker and the filter being well washed and the washings added to the filtrate. The filtrate and washings are then boiled, and whilst boiling 10 c.c. of a 5 per cent. solution of barium chloride is added, after which the boiling is continued for half an hour. The precipitated barium sulphate is filtered off and weighed in the usual manner and the amount calculated into sulphur.

Half-hydrated lime is made thus: Calcine a quantity of marble and divide the powder into two portions. To one of these add exactly the weight of water necessary to form $Ca(OH)_2$ and then mix with the other half.

APPENDIX

The following is a copy of a form issued by the Home Office, which should be mounted and hung in a prominent position in all tar distilleries :—

Form 939.

September, 1910.

FACTORY AND WORKSHOP ACT, 1901

Tar Distilling

The following directions are approved by the Home Office, and are applicable to factories in which is carried on the distillation of tar for the production of naphtha, light oil, creosote oil, and pitch.

Fencing

1. All uncovered tar reservoirs, wells and tanks, unless constructed so as to be at least three feet in height above the ground or platform, should be securely fenced, with either a brick wall or double rails, to the height of three feet.

Cleaning

2. During the process of cleaning, every tar still should be completely isolated from adjoining tar stills either by disconnecting the pipe leading from the swan neck to the condenser worm, or by disconnecting the waste gaspipe fixed to the worm end or receiver. Blank flanges should be inserted between the disconnections. In addition, the pit discharge pipe or cock at the bottom of the still should be disconnected.

Ventilation

3. Every tar still should be ventilated and allowed to cool before persons are allowed to enter.

Inspection

4. Every tar still should be inspected by the Foreman or other responsible person before any workman is allowed to enter.

5. The inspecting Foreman on first entering any tar still or tank, and all persons employed in tar stills or tanks in which there are no cross stays or obstructions likely to cause entanglement, should be provided with a belt securely fastened round the body with a rope attached, the free end being left with two men outside whose sole duty should be to watch and draw out any person appearing to be affected by gas. The belt and rope should be adjusted and worn in such a manner that the wearer can be drawn up head foremost and through the manhole and not across it.

Remedy for Gassing

6. A bottle of compressed oxygen, with mouthpiece, should be kept at all times ready for use ; and printed instructions as to the use of this bottle, and the method to be

employed for resuscitation by means of artificial respiration, should be kept constantly affixed. A draft of such instructions is appended.

Respirators

7. A supply of suitable chemical respirators properly charged and in good condition should be kept ready for use in case of emergency arising from sulphuretted hydrogen or certain poisonous gases. (Granules of carbon saturated with a solution of caustic soda readily absorb sulphuretted hydrogen and may be used for charging respirators.)

Lights

8. The use of naked lights should be strictly prohibited in any portion of the works where gas of an inflammable nature is liable to be given off.

Safety-Valve

9. Each still should be provided with a proper safety-valve, which should at all times be kept in efficient working condition.

B. A. WHITELEGGE,
Chief Inspector of Factories.

Home Office,
December, 1909.

GASSING

Symptoms.—The first symptoms are giddiness, weakness in the legs, and palpitation of the heart. If a man feels these he should at once move into fresh warm air, when he will quickly recover if slightly affected. He should avoid exposure to cold. He should not walk home too soon after recovery ; any exertion is harmful.

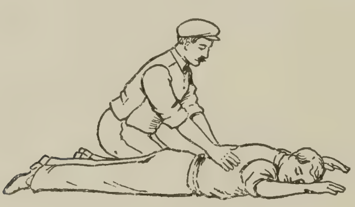

Diagram 1.

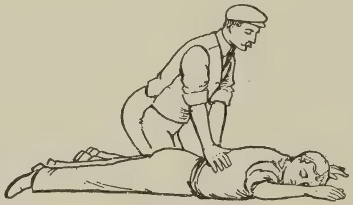

Diagram 2.

First Aid.—Remove the patient into fresh warm air. Send for the oxygen apparatus. Send for a doctor. Begin artificial breathing at once if the patient is insensible and continue it for at least half an hour, or until natural breathing returns. Give oxygen* at the same time and continue it after natural breathing returns.

Artificial Breathing (Schäfer Method).—Place the patient face downwards as shown in the diagrams.

Kneel at the side of the patient and place your hands flat in the small of his back with thumbs nearly touching, and the fingers spread out on each side of the body over the lowest ribs (see Diagram 1).

Then promote artificial breathing by leaning forward over the patient and, without violence, produce a firm, steady, downward pressure (see Diagram 2). Next release all pressure by swinging your body backwards without lifting your hands from the patient (see Diagram 1).

Repeat this pressure and relaxation of pressure without any marked pause between the movements, *about* 15 *times a minute*, until breathing is established.

*USE OF OXYGEN CYLINDER.—Open the valve gradually by tapping the lever key (which must first be extended to its full length) with the wrist, until the oxygen flows in a gentle stream from the mouthpiece into the patient's mouth. The lips should not be closed round the mouthpiece. The nostrils should be closed during breathing in, and opened during breathing out.

If the teeth are set, close the lips and one nostril. Let the conical end of the mouth-piece slightly enter the other nostril during breathing in, and remove it for breathing out.

The following are reproductions of the latest forms which should find place in tar distilleries and most gas works under the Factory and Workshop Act of 1901–20.

FORM 984.

July, 1922.

[*Form prescribed by the Secretary of State.*

FACTORY AND WORKSHOP ACT, 1901 TO 1920

CHEMICAL WORKS REGULATIONS, 1922

MADE BY THE SECRETARY OF STATE UNDER SECTION 79 OF THE FACTORY AND WORKSHOP ACT, 1901

In pursuance of Section 79 of the Factory and Workshop Act, 1901, I hereby make the following Regulations and direct that they shall apply to the manufactures and processes incidental thereto carried on in chemical works as hereinafter defined.

Provided that nothing in these Regulations shall apply to (*a*) the manufacture of certain compounds of lead, namely, any carbonate, sulphate, nitrate, or acetate of lead; (*b*) the manufacture of red or orange lead or of flaked litharge; (*c*) the manufacture and necessary purification of coal gas, water gas, and producer gas for lighting, heating, and power purposes; (*d*) the process of textile printing, bleaching, dyeing, mercerising, tanning and brewing; (*e*) the distillation of alcohol, of wood (except where acetic acid is isolated or manufactured), and of shale in the manufacture of crude shale oil; (*f*) processes carried on by way of experiment.

Regulations 2 (*b*) and 12, and, so far as concerns the processes of grinding or crushing caustic by machinery or packing ground caustic, making or packing of bleaching powder, distillation of gas or coal tar or any process in chemical manufacture in which gas or coal tar is used, the refining of crude shale oil and the manipulation of pitch, Regulations 26, 27, and 28 shall not come into force till 1st April, 1923, or such later date or dates as the Secretary of State may appoint, but save as aforesaid, all the Regulations shall take effect on 1st October, 1922. From that date the Regulations dated 30th December, 1908, for the manufacture of nitro and amido derivatives of benzene, and the Regulations dated 9th August, 1913, for the manufacture of chromate and bichromate of potassium or sodium shall be revoked.

These Regulations may be cited as the Chemical Works Regulations, 1922.

[1]*Definitions*

In these Regulations :—

Chemical works means any works or such parts of any works as are named in the Schedule of this Order.

Bleaching powder means the bleaching powder commonly called chloride of lime.

Chlorate means chlorate or perchlorate.

Caustic means hydroxide of potassium or sodium.

Caustic pot means a metal pot fixed over a furnace or flue and surrounded by brickwork, such as is commonly used for concentrating caustic liquor, whether such pot be used for concentrating or boiling caustic or other liquor.

Chrome process means the manufacture of chromate or bichromate of potassium or sodium, or the manipulation, movement or other treatment of these substances in connection with their manufacture.

Nitro or amido process means the manufacture of nitro or amido derivatives of phenol and of benzene or its homologues, and the making of explosives with the use of any of these substances.

Breathing apparatus means (1) a helmet or face-piece with necessary connections by means of which a person using it in a poisonous, asphyxiating, or irritant atmosphere breathes ordinary air, or (2) any other suitable apparatus approved in writing by the Chief Inspector of Factories.

Life-belt means a belt made of leather or other suitable material which can be securely fastened round the body, with a suitable length of rope attached to it, each of which is sufficiently strong to sustain the weight of a man.

Efficient exhaust draught means localised ventilation effected by mechanical or other means for the removal of gas, vapour, fume, or dust, which prevents it from escaping into the air of any place in which work is carried on.[2]

Surgeon means the Certifying Factory Surgeon of the District, or a duly qualified medical practitioner appointed by written certificate of the Chief Inspector of Factories, which appointment shall be subject to such conditions as may be specified in that certificate.

Suspension means suspension by written certificate in the Health Register, signed by the *Surgeon*, from employment in any process mentioned in the certificate.

Exceptions

Where it is proved to the satisfaction of the Chief Inspector of Factories that by reason of exceptional circumstances in any works subject to these Regulations, or by reason of the infrequency of the process, or for other reasons, all or any of the requirements of the Regulations are not necessary for the protection of persons employed in such works, he may by certificate in writing (which he may in his discretion revoke) exempt such works from all or any of the provisions of the same, subject to such conditions as he may by such certificate prescribe.

Duties

It shall be the duty of the occupier to comply with these Regulations, and it shall be the duty of all agents, foremen, and persons employed to conduct their work in accordance with these Regulations.

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[1] Terms to which defined meanings are given are printed throughout in italics.

[2] Care must be taken that the means provided do not cause a contravention of the provisions of the Alkali, etc., Works Regulation Act 1906. (6 Edw. 7. c. 14.)

PART I

Applying to all Chemical Works

1. With regard to every fixed vessel, whether pot, pan, vat, or other structure, containing any dangerous material, and not so covered as to eliminate all reasonable risk of accidental immersion of any portion of the body of a person employed :—

(*a*) Each such vessel shall, unless its edge is at least 3 feet above the adjoining ground or platform, be securely fenced to a height of at least 3 feet above such adjoining ground or platform.

(*b*) No plank or gangway shall be placed across or inside any such vessel unless such plank or gangway is—

- (i) at least 18 inches wide ; and
- (ii) securely fenced on both sides ; either by upper and lower rails, to a height of 3 feet, or by other equally efficient means.

(*c*) Where such vessels adjoin, and the space between them, clear of any surrounding brick or other work, is either

- (i) less than 18 inches in width, or
- (ii) is 18 or more inches in width, but is not securely fenced on both sides to a height of at least 3 feet,

secure barriers shall be so placed as to prevent passage between them.

Provided that paragraph (*a*) of this Regulation shall not apply to that part of the sides of brine evaporating pans at which raking, drawing or filling is carried on, or to saturators used in the manufacture of sulphate of ammonia.

2. The following processes shall not be carried on except under an *efficient exhaust draught* :—

(*a*) drawing a charge from a salt cake furnace ;

(*b*) slaking of lime for use in a chemical process except when it is carried on in the open air or by means of an enclosed mechanical or other appliance so constructed as to prevent the escape of steam or dust into the air of any place in which any person is employed ;

(*c*) any process involving action of acid or alkali on metal whereby there is a liability to the evolution of arseniuretted hydrogen.

3. All mills and screens for grinding and screening anhydrous lime, and all mechanica conveyors used in connection therewith, shall be so enclosed as to prevent the escape of dust.

4.—(*a*) All places in which persons are employed and all means of access thereto shall be sufficiently lighted by day and by night.

(*b*) No electric arc lamp, or naked light, fixed or portable, shall be used, and no person shall have in his possession any lucifer match or any apparatus of any kind for producing a naked light, or spark in, on, or about any part of the works where there is liability to explosion from inflammable gas, vapour or dust, and all incandescent electric lights in such parts shall be in double air-tight glass covers.

(*c*) Stoves shall not be used for the artificial heating of places in which there is danger of ignition of gas, vapour, or dust ; if steam pipes or radiators are used for this purpose they shall be placed so that there is a space of not less than two inches between them and the wall, and shall be protected by a wire screen.

(*d*) A prominent notice, legible by day and by night, prohibiting smoking or the use of naked lights, and the carrying of matches, or any apparatus for producing a naked light or spark, shall be affixed at the entrance of every room or place in which there is liability to explosion from inflammable gas, vapour, or dust.

5. Every still and every closed vessel in which gas is evolved or into which gas is passed, and in which the pressure is liable to rise to a dangerous degree, shall have attached to it, and maintained in proper condition, a proper safety-valve or other equally efficient means to relieve the pressure.

Nothing in this Regulation shall apply to metal bottles or cylinders used for the transport of compressed gases.

6. There shall be provided in every works where dangerous gas or fume is liable to escape a sufficient supply of :—

(*a*) *Breathing apparatus.*
(*b*) Oxygen and suitable means for its administration.
(*c*) *Life-belts.*

The *breathing apparatus* and other appliances required by this Regulation shall be maintained in good order and kept in an ambulance room or in some other place approved in writing by the District Inspector of Factories, which shall be conveniently situated. In every such room or place and wherever required in writing by the District Inspector of Factories there shall be affixed the official cautionary notice regarding gassing and burns.

Such apparatus and appliances shall be inspected once every month by a competent person, conversant with their use, appointed by the occupier, and a record of their condition shall be entered in a book provided for that purpose, which shall be produced when required by an Inspector.

7. Before any person enters, for any purpose except that of rescue, any absorber, boiler, culvert, drain, flue, gas purifier, sewer, still, tank, tower, vitriol chamber, or other place where there is reason to apprehend the presence of dangerous gas or fume, a responsible person appointed by the occupier for the purpose shall personally examine such place and shall certify in writing in a book to be kept for the purpose either that such place is isolated and sealed from every source of such gas or fume and is free from danger, or that it is not so isolated and sealed and free from danger. No person shall enter any such place which is certified not to be so isolated and sealed and free from danger unless he is wearing a *breathing apparatus*, and (where there are no cross-stays or obstructions likely to cause entanglement) a *life-belt*, the free end of the rope attached to which shall be left with a man outside, whose sole duty shall be to keep watch and to draw out the wearer if he appears to be affected by gas or fume. The belt and rope shall be so adjusted and worn that the wearer can be drawn up head foremost through any manhole or opening.

8. No person shall enter any place mentioned in Regulation 7 for the purpose of rescue unless he is wearing a *breathing apparatus* and a *life-belt* in the manner specified in that Regulation.

9. A sufficient supply of non-metallic spades, scrapers and pails shall be provided for the use of persons employed in cleaning out or removing the residues from any chamber, still, tank, or other vessel which has contained sulphuric or hydrochloric acid or other substance which may cause evolution of arseniuretted hydrogen.

10. In all places where strong acids or dangerous corrosive liquids are used—

(*a*) there shall be provided, for use in case of emergency :—

(i) Adequate and readily accessible means of drenching with cold water persons, and the clothing of persons, who have become splashed with such liquid ;

(ii) A sufficient number of eye-wash bottles, filled with distilled water or other suitable liquid, kept in boxes or cupboards conveniently situated and clearly indicated by a distinctive sign which shall be visible at all times.

(*b*) Except where the manipulation of such acids and liquids is so carried on as to prevent risk of personal injury from splashing or otherwise, there shall be provided for those who have to manipulate such acids or liquids, sufficient and suitable goggles and gloves or other suitable protection for the eyes and hands. If gloves are provided they shall be collected, examined and cleaned at the close of the day's work and shall be repaired or renewed when necessary.

(*c*) There shall be kept affixed the official cautionary notice regarding gassing and burns.

11. There shall be provided in readily accessible positions a sufficient number of " First Aid " boxes or cupboards.

Each " First Aid " box or cupboard shall be distinctively marked, and if newly provided after the date of these Regulations shall be marked plainly with a white cross on a red ground, and shall contain, besides any other medical appliances or requisites :—

(i) A supply of suitable sterilised dressings for fingers, hands, feet, or other injured parts.
(ii) A supply of sterilised cotton-wool.
(iii) A supply of sterilised burn dressings (large and small).
(iv) Plaster—waterproofed on the outside.
(v) Ointment, a 2 per cent. alcoholic solution of iodine and a bottle of sal volatile.
(vi) A copy of the First Aid leaflet issued by the Factory Department of the Home Office.

Nothing except appliances or requisites for First Aid shall be kept in a " First Aid " box or cupboard.

Each " First Aid " box shall be kept stocked and in good order, and shall be placed in the charge of a responsible person, who shall always be readily available during working hours.

A notice or notices shall be affixed in every workplace stating the name of the person in charge of the " First Aid " box or cupboard provided in respect of that place.

12. There shall be provided and maintained in good order in every works in which the total number of persons employed in the processes to which these Regulations apply at any one time is 250 or more, an Ambulance room.

The Ambulance room shall be a separate room used only for the purpose of treatment and rest. It shall have a floor space of not less than 100 square feet and smooth, hard and impervious walls and floor, and shall be provided with ample means of natural and artificial lighting. It shall contain at least :—

(i) A glazed sink with hot and cold water always available.
(ii) A table with a smooth top.
(iii) Means for sterilising instruments.
(iv) A supply of suitable dressings, bandages and splints.
(v) A couch.
(vi) A stretcher.

Where persons of both sexes are employed, arrangements shall be made at the Ambulance room for their separate treatment.

The Ambulance room shall be placed under the charge of a qualified nurse, or other person trained in First Aid, who shall always be readily available during working hours and shall keep a record of all cases of accidents or sickness treated in the room.

13. At every works there shall be provided and maintained in good condition a suitably constructed ambulance carriage, for the purpose of the removal of serious cases of accident or sickness, unless arrangements have been made for obtaining such a carriage when required from a hospital or other place in telephonic communication with the works.

14. Arrangements shall be made to the satisfaction of the Chief Inspector of Factories for the effective training and practising of a sufficient number of persons in the use of the appliances required by Regulation 6 and in administering First Aid.

15. There shall be provided for all female persons employed whose work is done standing, facilities for sitting, so as to enable them to take advantage of any opportunities for resting which may occur in the course of their employment.

16. There shall be provided and maintained at suitable points, conveniently accessible at all times to all persons employed :—

(*a*) An adequate supply of wholesome drinking water from a public main or from some other source of supply approved in writing by the local authority of the district in which the factory is situated, which shall be either laid on, or contained in a suitable vessel ;

(*b*) (except where the water is delivered in an upward jet from which the workers can conveniently drink) at least one suitable cup or drinking vessel at each point of supply, with facilities for rinsing it in drinking water.

Each drinking water supply shall be clearly marked " Drinking Water."

All practicable steps shall be taken to preserve the water and vessels from contamination.

17. (1) Every person employed shall—

(*a*) report to his foreman any defect in any fencing, *breathing apparatus*, appliance or other requisite provided in pursuance of these Regulations, as soon as he becomes aware of such defect ;

(*b*) use the articles, appliances or accommodation required by these Regulations for the purpose for which they are provided ;

(*c*) wear the *breathing apparatus* and *life-belt* where required under Regulations 7 and 8.

(2) No person shall—

(*a*) remove any fencing provided in pursuance of Regulation 1 unless duly authorised ; or

(*b*) stand on the edge or on the side of any vessel to which Regulation 1 applies ;

(*c*) pass or attempt to pass any barrier erected in pursuance of Regulation 1 (*c*) ;

(*d*) place across or inside any vessel to which Regulation 1 applies any plank or gangway which does not comply with Regulation 1 (*b*), or make use of any such plank or gangway while in such position ;

(*e*) take a naked light or any lamp or matches or any apparatus for producing a naked light or spark into, or smoke in, any part of the works where there is liability to explosion from inflammable gas, vapour or dust ;

(*f*) use a metal spade, scraper or pail when cleaning out or removing the residues from any chamber, still, tank, or other vessel which has contained sulphuric acid or hydrochloric acid or other substance which may cause evolution of arseniuretted hydrogen ;

(*g*) remove from a First Aid box or cupboard or from the Ambulance room any First Aid appliance or dressing except for the treatment of injuries in the works.

PART II

Applying to Works or Parts thereof in which—

I. *Caustic pots* are used ; or

II. *Chlorate* or *bleaching powder* is manufactured ; or

III.—(*a*) Gas tar or coal tar is distilled or is used in any process of chemical manufacture ; or

  (*b*) A *nitro or amido process* is carried on ; or

  (*c*) A *chrome process* is carried on ; or

IV. Crude shale oil is refined or processes incidental thereto are carried on ; or

V. Nitric acid is used in the manufacture of nitro compounds.

18. Every *caustic pot* shall be of such construction that there shall be no foothold on the top or sides of the brickwork or flues ; and the edge of every such pot constructed, rebuilt or replaced after these Regulations come into force shall be at least 3 feet in height above the adjoining ground or platform.

19. Before any person enters a gas tar or coal tar still for any purpose except that of rescue, it shall be completely isolated from adjoining tar stills, either by disconnecting—

(*a*) the pipe leading from the swan neck to the condenser worm, or

(*b*) the waste gas pipe fixed to the worm end or receiver ; and

in addition, blank flanges shall be inserted between the disconnected parts, and the pitch discharge pipe or cock at the bottom of the still shall be disconnected.

20. No person shall enter a chamber for the purpose of withdrawing the charge of *bleaching powder* unless and until

(i) The chamber is efficiently ventilated, and

(ii) The air in the chamber has been tested and found to contain not more than 2·5 grains of free chlorine gas per cubic foot.

A register containing details of all such tests shall be kept in a form approved by the Chief Inspector of Factories.

21. In a *nitro or amido process* :—

(*a*) If crystallised substances are broken or any liquor agitated by hand, means shall be taken to prevent, as far as practicable, the escape of dust or fume into the air of any place in which any person is employed. The handles of all implements used in the operations shall be cleansed daily.

(*b*) Cartridges shall not be filled by hand except by means of a suitable scoop.

(*c*) Every drying stove shall be efficiently ventilated to the outside air in such a manner that hot air from the stove shall not be drawn into any workroom.

(*d*) No person shall enter a stove to remove the contents until a free current of air has been passed through it.

(*e*) Every vessel containing nitro or amido derivatives of phenol or of benzene or its homologues shall, if steam is passed into or around it, or if the temperature of the contents be at or above the temperature of boiling water, be covered in such a way that steam or vapour shall be discharged into the open air at a height of not less than 25 feet from the ground or the working platform, and at a point where it cannot be blown back again into the workroom.

(*f*) In every room in which dust is generated or fume is evolved an *efficient exhaust draught* shall be provided.

22.—(*a*) Every machine used for grinding or crushing *caustic* shall be enclosed, and

(*b*) Where any of the following processes are carried on :—

(i) Grinding or crushing of *caustic ;*
(ii) Packing of ground *caustic ;*
(iii) Grinding, sieving, evaporating or packing in a *chrome process ;*
(iv) Crushing grinding or mixing of material or cartridge filling in a *nitro or amido process ;*

an *efficient exhaust draught* shall be provided.

23.—(*a*) *Chlorate* shall not be crystallised, ground or packed except in a room or place not used for any other purpose, the floor of which room or place shall be of cement or other smooth, impervious and incombustible material, and shall be thoroughly cleansed daily.

(*b* Wooden vessels shall not be used for the crystallisation of *chlorate*, or to contain crystallised or ground *chlorate ;* provided that this Regulation shall not prohibit the packing of *chlorate* for sale into wooden casks or other wooden vessels.

24. No person under 18 years of age shall be employed in a *chrome process* or in a *nitro or amido process*.

25.—(*a*) There shall be provided and maintained for the use of all persons employed in :—

(i) A *nitro or amido process*, sufficient and suitable overalls or suits of working clothes and sufficient and suitable protective footwear ; [1]
(ii) grinding raw materials in a *chrome process*, sufficient and suitable overall suits ;
(iii) the crystal department and in packing in a *chrome process*, sufficient and suitable protective coverings ;
(iv) packing in a *chrome process*, sufficient and suitable respirators ;
(v) any room or place in which *chlorate* is crystallised, ground or packed, clothing of woollen material and boots or overshoes, the soles of which shall have no metal on them ;
(vi) any room or place in which *caustic* is ground or crushed by machinery, sufficient and suitable goggles and gloves, or other suitable protection for the eyes and hands ;
(vii) *bleaching powder* chambers, or in packing charges drawn from such chambers, a supply of flannel or other suitable respirators.

(*b*) (i) The overalls or suits of working clothes required to be provided by

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[1] In those places to which the Explosives Act, 1875 (38-9 V. c. 17), applies, the provision made must conform to the requirements of that Act.

(*a*) (i) and (ii) of this Regulation shall be washed, cleansed or renewed at least once every week ;

(ii) the filtering material of the respirators required to be provided by (*a*) (iv) of this Regulation shall be washed or renewed daily ;

(iii) the woollen clothing required to be provided by (*a*) (v) of this Regulation shall not be removed from the works for any purpose, but shall be washed daily after use and thoroughly dried before being worn again ; all such clothing when worn out shall be destroyed ;

(iv) if gloves are provided to comply with (*a*) (vi) of this Regulation, they shall be collected, examined and cleaned at the close of the day's work, and shall be repaired or renewed when necessary.

26. There shall be provided and maintained for the use of all persons for whom overalls or suits of working clothes are required to be provided under Regulation 25 (*a*) :—

(*a*) A suitable cloakroom for clothing put off during working hours, with adequate arrangements for drying the clothing if wet ; and

(*b*) a suitable place, or places, separate from the cloakroom and from the meal room provided in pursuance of Regulation 27, for the storage of overalls or working suits.

The accommodation so provided thall be placed under the charge of a responsible person, and shall be kept clean.

27. There shall be provided and maintained for the use of all persons remaining on the premises during the meal intervals, who are employed in (*a*) any *nitro or amido process*, (*b*) any *chrome process*, (*c*) grinding or crushing *caustic* by machinery or packing of ground *caustic*, (*d*) making or packing of *bleaching powder*, including the drawing of the charges from the chambers, (*e*) crystallising, grinding or packing of *chlorate*, (*f*) distilling gas tar or coal tar (other than blast furnace tar), or in any process of chemical manufacture in which gas or coal tar (other than blast furnace tar) is used, or (*g*) refining of crude shale oil, suitable and adequate messroom or canteen accommodation, which shall be furnished with—

(i) sufficient tables or benches with back rests ;

(ii) adequate means for cooking or warming food and for boiling water ; and

(iii) arrangements for washing crockery and utensils.

The messroom shall be sufficiently warmed for use during meal intervals, be placed under the charge of a responsible person and be kept clean and well ventilated.

28. There shall be provided and maintained in a cleanly state and in good repair for the use of all persons employed in (*a*) any *nitro or amido process ;* (*b*) any *chrome process ;* (*c*) grinding or crushing *caustic* by machinery or packing of ground *caustic ;* (*d*) making or packing of *bleaching powder*, including the drawing of the charges from the chambers ; (*e*) crystallising, grinding or packing of *chlorate ;* (*f*) distilling gas tar or coal tar (other than blast furnace tar), or in any process of chemical manufacture in which gas or coal tar (other than blast furnace tar) is used ; (*g*) the manipulation of pitch (other than blast furnace pitch) ; or (*h*) refining of crude shale oil :—

A lavatory, under cover, with a sufficient supply of clean towels, renewed daily, and of soap and nail brushes, and with either—

(*a*) a trough with a small impervious surface, fitted with a waste pipe without plug, and of such length as to allow at least two feet for every five such persons, and having a constant supply of warm water from taps or jets above the trough at intervals of not more than two feet; or

(*b*) at least one lavatory basin for every five such persons, fitted with a waste pipe and plug or placed in a trough having a waste pipe, and having either a constant supply of hot and cold water or warm water laid on, or (if a constant supply of heated water be not reasonably practicable) a constant supply of cold water laid on and a supply of hot water always at hand when required for use by persons employed.

29. There shall be provided for the use of all persons employed in (*a*) a *nitro or amido process,* (*b*) the crystal department and the packing room in a *chrome process,* (*c*) the process of distilling gas or coal tar (other than blast furnace tar) and any process of chemical manufacture in which such tar is used and (*d*) refining of crude oil shale :—

Sufficient and suitable bath accommodation (douche or other), with hot and cold water laid on and a sufficient supply of soap and towels.

A bath register shall be kept containing a list of all persons employed in the above processes and an entry of the date when each person takes a bath.

30. In a *chrome process* and in a *nitro or amido process :*—

(*a*) A Health Register, containing the names of all persons employed, shall be kept in a form approved by the Chief Inspector of Factories.

(*b*) No person shall be newly employed for more than fourteen days without a certificate of fitness granted after examination by the *Surgeon* by signed entry in the Health Register.

(*c*) Every person employed shall be examined by the *Surgeon* once in each calendar month (or at such intervals as may be prescribed in writing by the Chief Inspector of Factories) on a date or dates of which due notice shall be given to all concerned.

(*d*) Every person employed shall present himself at the appointed time for examination by the *Surgeon* as provided in (*b*) and (*c*) of this Regulation.

(*e*) The *Surgeon* shall have power of *suspension* as regards all persons employed, and no person after *suspension* shall be employed without written sanction from the *Surgeon* entered in the Health Register.

(*f*) No person shall introduce, keep, prepare or partake of any food, drink or tobacco in any room or place in which a *nitro or amido process* is carried on, or in the crystal department of a *chrome process.*

31. Every person employed—

(*a*) in a process to which Regulation 25 (*a*) applies shall wear the protective clothing, footwear, respirators, goggles or gloves provided under Regulation 25 (*a*) and shall deposit overalls or suits of working clothing so provided, as well as clothing put off during working hours, in the places provided under Regulations 26 (*a*) and (*b*);

(*b*) in processes to which Regulation 28 applies shall carefully wash the hands and face before partaking of any food or leaving the premises;

(*c*) in any processes to which Part II of these Regulations apply shall use the protective appliances supplied in respect of any process in which he is engaged.

EDWARD SHORTT,
One of His Majesty's Principal Secretaries of State.

HOME OFFICE, WHITEHALL,
11*th July*, 1922.

SCHEDULE

Chemical works means any works or that part of a works in which :—

1. The manufacture or recovery of any of the following is carried on :—
    - (*a*) Carbonates, chromates, chlorates, oxides or hydroxides of potassium, sodium, iron, aluminium, cobalt, nickel, arsenic, antimony, zinc or magnesium.
    - (*b*) Ammonia and the hydroxide and salts of ammonium.
    - (*c*) Sulphurous, sulphuric, nitric, hydrochloric, hydrofluoric, hydriodic, hydrosulphuric, boric, phosphoric, arsenious, arsenic, lactic, acetic, oxalic, tartaric or citric acids and their metallic or organic salts, and
    - (*d*) Cyanogen compounds.
2. A wet process is carried on
    - (*a*) For the extraction of metal from ore or from any by-product or residual material ; or
    - (*b*) In which electrical energy is used in any process of chemical manufacture.
3. Alkali waste or the drainage therefrom is subjected to any chemical process for the recovery of sulphur, or for the utilisation of any constituent of such waste or drainage.
4. Carbon bisulphide is made or hydrogen sulphide is evolved by the decomposition of metallic sulphides, or hydrogen sulphide is used in the production of such sulphides.
5. Bleaching powder is manufactured or chlorine gas is made or is used in any process of chemical manufacture.

6.—(*a*) Gas tar or coal tar or any compound product or residue of such tars is distilled or is used in any process of chemical manufacture.
    (*b*) Synthetic colouring matters or their intermediates are made.

7. The refining of crude shale oil or processes incidental thereto are carried on.
8. Nitric acid is used in the manufacture of nitro compounds.
9. Explosives are made with the use of nitro compounds.

NOTE

Breach of Regulations.—(1) If any occupier, owner or manager, who is bound to observe any regulation under this Act, acts in contravention of, or fails to comply with the regulation, he shall be liable for each offence to a fine not exceeding ten pounds and, in the case of a continuing offence, to a fine not exceeding two pounds for every day during which the offence continues after conviction therefor.

(2) If any person other than an occupier, owner or manager, who is bound to observe any regulation under this Act, acts in contravention of, or fails to comply with, the regulation, he shall be liable for each offence to a fine not exceeding two pounds ; and the occupier of the factory or workshop shall also be liable to a fine not exceeding ten pounds, unless he proves that he has taken all reasonable means by publishing, and to the best of his power enforcing, the regulations to prevent the contravention or non-compliance (s. 85).

Publication of Regulations.—Printed copies of all regulations for the time being in force under this Act in any factory or workshop shall be kept posted up in legible characters in conspicuous places in the factory or workshop where they may be conveniently read by the persons employed.

A printed copy of all such regulations shall be given by the occupier to any person affected thereby on his or her application.

Every person who pulls down, injures or defaces any regulations posted up in pursuance of this Act, or any notice posted up in pursuance of the regulations, shall be liable to a fine not exceeding five pounds (s. 86).

Form 395.
January, 1922.

Form prescribed by the
Secretary of State.

CAUTION

DANGERS FROM GASSING OR BURNS

(Official Cautionary Notice under the Chemical Regulations.)

EVERY PERSON EMPLOYED ON THIS PLANT SHOULD READ THIS NOTICE CAREFULLY.

VALUABLE TIME WILL BE LOST IF YOU WAIT TO READ IT UNTIL AN ACCIDENT HAPPENS.

Dangers from Gassing.

AN ACCIDENT TO THE PLANT IN THIS DEPARTMENT MAY CAUSE AN ESCAPE OF GAS OR FUMES.

Remember that some of the dangerous gases cannot be seen or smelt.

Every worker should learn :—

1. Where the Breathing Apparatus is kept.
2. How to use it.
3. When to use it.
4. The signs of gassing.
5. How to perform Artificial Respiration.

Except when attempting to rescue someone, do not enter any part of the works or plant where you have reason to suspect that dangerous gas or fume is present until it has been examined by the responsible official appointed by the occupier.

USE OF BREATHING APPARATUS AND LIFE-BELT

Always wear the breathing apparatus and life-belt with rope attached

When attempting to rescue anyone ; or
When entering any place which is certified to be dangerous.

The Breathing Apparatus and Life-belt for this Department are kept at...........

Learn to put on the Breathing Apparatus quickly and correctly. By doing so you may be able to save a life.

SYMPTOMS

Effects of gassing (apart from headache, giddiness, pain in the stomach and smarting of the eyes) are :—

1. Feeling of loss of power.
2. Difficulty in breathing.

If you feel any of these effects
Warn your mates.
Go into the fresh air *at once.*
Avoid exertion for some hours even if only slightly gassed.

If a fellow-worker is gassed *send at once for a Doctor* and *immediately commence* the following treatment :—

GENERAL TREATMENT

1. Remove the patient into the fresh air and loosen clothing at waist and neck.
2. Keep him lying down.
3. Cover him with a blanket and keep him warm.
4. *Do not* give stimulants. When a patient is able to swallow give *Hot Coffee*

If breathing is shallow (weak) or has stopped :—

5. Apply Artificial Respiration and give Oxygen.
6. *When Natural Breathing starts* leave off Artificial Respiration but *continue* giving Oxygen.

Do *not* let a patient walk home when better. Send for an Ambulance to take him home.

Nitrous Fumes.—The effects of these reddish brown fumes (shortness of breath and cough) may not come on for some hours after they have been breathed.

If affected at home Send at once for a doctor.
Keep warm in a well-ventilated room.
If affected at work Apply the *General Treatment* given above.
In addition
If patient is blue in the face, give Oxygen.
If patient is *conscious*, give a dose of the gas mixture.[1]

Chlorine.—This gas cannot be breathed without causing severe pain in the chest.
Apply the *General Treatment* as above.
In addition allow patient to smell carbonate of ammonia.

Sulphurous Fumes.—Apply the *General Treatment* as above.
In addition give a seidlitz powder.

Sulphuretted Hydrogen.
Benzene and Similar Volatile Bodies.
Carbon Monoxide or Producer Gas.
Carbon Dioxide.

Apply the *General Treatment.* Give Oxygen freely. Keep on Artificial Respiration for at least an hour.

HOW TO APPLY ARTIFICIAL RESPIRATION

Place the patient face downwards as shown in the diagrams.[2]

Kneel astride or at the side of the patient and place your hands flat in the small of his back with thumbs nearly touching, and the fingers spread out on each side of the body over the lowest ribs. (See Diagram 1.)[2]

Then promote artificial breathing by leaning forward over the patient, and without violence produce a firm, steady, downward pressure. (See Diagram 2.)[2] Next, release all pressure by swinging your body backwards without lifting your hands from the patient. (See Diagram 1.)[2]

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[1] GAS MIXTURE.—Ammon. carb. gr. 120. Tinct. scillae. m. 90. Sp. chlorof. m. 120. Vin. ipec. m. 150. Tinct. senegae. m. 90. Aq. ad. 6 oz. Dose: One tablespoonful, to be repeated if necessary.

[2] Not reproduced here.

Repeat this pressure and relaxation of pressure, without any marked pause between the movements, *about fifteen times a minute,* until breathing is established.

CHEMICAL BURNS

OF THE SKIN.	1. Immediately flood with clean water or plunge burnt part into a bucket or tub filled with clean water. 2. Cover the burn with a burn dressing from the First Aid box.
OF THE EYE.	1. Wash out the eye by gently blowing a stream of water from the eye-wash bottle; *or* immerse the face in a basin of clean water and open and shut the eyes. 2. *Report to a Doctor immediately.*

SPLASHES OF ANILIN OR NITRO-BENZENE

These can enter the system when they touch or wet the skin.
If the clothing is splashed sufficiently to wet the skin :—

1. Remove the clothing *at once.*
2. Wash the skin well; take a bath if necessary.

SAFETY FIRST

LIVES can be saved by wearing the *Breathing Apparatus and Life-belt.*
EYES can be saved by wearing *Goggles.*

For rescue work the "Salvus" half-hour breathing apparatus or the "Antipoys" short-distance breathing apparatus will be found suitable, the former being perhaps the most suitable. In the work of resuscitation, oxygen can be administered simply and most effectively by employing the "Novita" reviving apparatus. The Schaefer method of artificial respiration can be used in conjunction with this apparatus.

The following particulars relating to sulphuretted hydrogen (SH_2), and carbon monoxide (CO), published by "Mentor" in *The Gas World* of November 21, 1908, will prove useful to those interested in tar distillation :—

Symptoms of Poisoning by Carbon Monoxide

Usually the first thing noticed by a person who is moving about and has inhaled the gas is a tendency to palpitation, dizziness or faintness and shortness of breath after exertion, following which there is a general weakening of the muscular, mental and sensory faculties. The patient is usually drowsy. When the blood has become about 50 per cent. saturated it is hardly possible for one to stand upright or walk, and with higher degrees of saturation the mental and muscular enfeeblement becomes more and more pronounced. One noteworthy point in connection with carbon monoxide poisoning is that very little actual distress results from the inhalation of the gas. After paralysis of the limbs, the senses gradually become more and more benumbed, as they would be by the administration of a gentle anæsthetic. With less than 1 per cent. of CO in the air, death is very gradual and peaceful, and with more than 1 or 2 per cent., loss of consciousness is usually followed by convulsions, and death rapidly ensues.

Symptoms Produced by Poisoning from SH_2

The symptoms produced by SH_2 poisoning are due to two causes: (1) its direct irritant action on the eyes and air passages, and (2) its intensely poisonous action, when absorbed, on the brain, heart, etc. Exposure to an atmosphere containing 0·01 to 0·02 per cent. soon produces inflammation of the eyes, and headache. Pain in the eyes often comes some time after the exposure, and with great severity, and may recur at intervals for several days. With 0·05 of SH_2, giddiness and other alarming symptoms show themselves, as well as great irritation of the eyes, nose, etc.

Tables showing the Poisonous Effects of Varying Percentages of CO and SH_2 on Human Beings

CARBON MONOXIDE

Percentage of gas present.				Effect on Human Beings.
Pure CO.	Coal gas containing 7 per cent. CO.	Carburetted water gas, 30 per cent. CO.	Pure Carburetted water gas containing 32 per cent. CO.	
0·05	0·7	0·17	0·1	After half an hour to two hours, giddiness on exertion.
0·1	1·4	0·30	0·2	Do., do., inability to walk.
0·2	2·8	0·66	0·4	Do., do., loss of consciousness, and perhaps final death.
0·4	5·6	1·3	0·8	Do., do., probable death.
1·0	14·0	3·3	2·0	After a few minutes, loss of consciousness, followed before long by death.

SULPHURETTED HYDROGEN

Percentage of SH_2 present.	Effect on Human Beings
0·001	Strong smell of rotten eggs.
0·02	After a few minutes, irritation of the nose, throat and eyes, accompanied by coughing.
0·05	Much irritation of the eyes and throat, giddiness and headache.
0·07	Death after several hours' exposure.
0·2	Death in about one and a half minutes.

The use of Oxygen in Cases of Gassing, How it is Administered, and How Long it Should be Given

Oxygen is a valuable aid to recovery in cases of poisoning from carbon monoxide. It should therefore always be kept ready on a gasworks. The oxygen is compressed and stored in strong steel cylinders, usually holding 20 cubic feet. The cylinder should be provided with a piece of india-rubber tubing at the end of which is a metal mouthpiece. The valve on the cylinder should be opened to the extent necessary to allow sufficient oxygen to issue to allow of its being inhaled " neat," or without much admixture with air. The mouthpiece is then placed loosely in the mouth, so that inhalation may proceed without distending the lungs. If the person is unconscious, the nostrils should be closed, by pinching them with the fingers, during the process of inhaling, and left free during the act of expiration. The time during which oxygen is administered should be at least ten minutes.

Carbon Monoxide Poisoning

In addition to the preceding notes on this subject, the following may be interesting·

The chances of poisoning by carbon monoxide are far greater in a gasworks than in a tar distillery, but as this volume will no doubt be read by workers employed in both of these factories, the author thinks it wise to say something upon this subject.

In the year 1921, there were 77 cases of carbon monoxide poisoning in England and Wales, 14 of which resulted in death.[1]

It is curious to note that some people are able to tolerate small doses of carbon monoxide without any apparent symptoms of ill-health, but this fact will not prevent such a person from becoming poisoned should larger quantities of gas be inhaled. In other cases toleration never becomes established and symptoms of illness begin to develop which gradually become worse, and it is the latter condition—that of non-toleration—which is very much more common. A very early symptom, and one which is fairly general, is that of intolerable headache which, should it become severe, will produce nausea and vomiting ; at times the headache does not develop until the affected person gets into the fresh air. In most cases of carbon monoxide poisoning attacks of giddiness are common, the patient seemingly losing partial control over the lower limbs. The digestive system is very frequently disorganised and stomach affections are quite common. The heart is often affected, and so may be the senses of smell, taste, sight, and hearing. Many patients become sleepy, feeling fatigued on the slightest exertion, and often develop impaired memories.

The treatment of carbon monoxide poisoning requires promptitude and care. The cause of poisoning is due to the fact that carbon monoxide has the power of combining with the hæmoglobin of the blood, and even of replacing the oxygen of oxyhæmoglobin which occurs in normal blood and is a combination of oxygen and hæmoglobin. The substance formed is known as carboxy-hæmoglobin, and it is carried to the various parts of the human system in the blood stream. It appears that oxygen is very easily split off from the hæmoglobin molecule, whereas carbon monoxide is only removed with comparative difficulty. On this account the blood is robbed to a lesser or greater extent of its oxygen-carrying capacity, and therefore the patient should be at once removed from the foul atmosphere into the fresh air. In carbon monoxide poisoning the blood takes on a bright cherry-red colour, and it will not coagulate.

As the general vitality of the patient will be lowered, it is very necessary indeed to keep him warm, and this must be done by applying hot-water bottles and warm blankets to the lower parts of the body and the lower limbs.

The position of the insensible patient is a matter of importance, particularly as the nervous system is most seriously affected owing to the fact that the blood is deprived of the greater part of its oxygen. The case is, as a matter of fact, one very similar to that of a person who has lost a considerable amount of blood. The patient should be placed upon his back with his limbs raised and his head low.

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[1] Annual Report of the Chief Inspector of Factories for the year 1921.

Artificial respiration should be then commenced and persisted in until breathing becomes sufficiently deep to enable the patient to inhale considerable amounts of pure air, the oxygen of which will enable the blood to give up the carbon monoxide combined with the hæmoglobin and replace it by oxygen.

It is as a rule wise to administer oxygen during artificial respiration ; the method by which this is done is described on page 479. It has been recommended by some that a certain proportion of carbon dioxide (5 per cent.) be administered with the oxygen. This recommendation apparently has emanated from an opinion held by Mosso that Cheyne-Stokes' breathing (which often occurs in carbon monoxide poisoning) was due to diminution of carbon dioxide generation in the blood. An administration of this nature must, of course, be carried out under the recommendation and supervision of a medical attendant.

After the patient has returned to consciousness it is absolutely necessary that he be allowed to rest and be treated also for shock. He should not be allowed to exert himself by walking, and if the case necessitates immediate removal to a hospital or to the home, then he may be removed in a suitable conveyance.

Sulphuretted Hydrogen Poisoning

Sulphuretted hydrogen acts upon the hæmoglobin of the red blood corpuscules, forming sulphur-methæmoglobin. The blood is dark in colour and remains fluid. It is on record that the breathing of an atmosphere only slightly impregnated with this gas may, if continued for a lengthy period, seriously affect the health and even cause death. Constant exposure to an atmosphere containing a very small quantity of sulphuretted hydrogen will produce headache, dullness, giddiness, loss of energy, local irritation of the eyes, indicated by pain and congestion of the conjuctiva, sneezing and irritation of the mucous membranes of the nose, and soreness of the mouth and throat. Often there are severe pains in the head and diffused pains in the abdomen. If inhaled in the concentrated form sulphuretted hydrogen is almost immediately fatal ; consciousness is lost at once and in a few seconds respiration ceases. If breathed in a less concentrated form, immediate unconsciousness may occur, which may last for several hours and finally pass into fatal coma. Tetanus with delirium or violent convulsions may become evident. Death is brought about by it directly affecting the normal functions of the central nervous system.

Poisoning by Benzene

Although poisoning by benzene (benzole) and vapours from light coal tar distillates is not common in this country, it is as well that attention be called to the risk. In the Annual Report of the Chief Inspector of Factories for the year 1921, 11 cases of poison are recorded against benzole, naphtha, and aniline ; unfortunately it does not say how many of these cases are due to benzole and naphtha. The author has had three or four cases occur in his experience, but in each instance complete recovery resulted after treatment by artificial respiration in the fresh air. It appears that benzene is somewhat more toxic than commercial benzole, commercially pure benzole coming in between these two materials. Undoubtedly the increase in toxicity is due to the more volatile nature of the purer products. Susceptibility to poisoning by these materials seems to rest in the very young and the old, and it appears that the female is more susceptible than the male. Various organic diseases increase susceptibility very materially, especially those affecting the kidneys and heart, and it should also be noted that individuals of a muscular build possessing rapid blood circulation, and who breathe deeply, more rapidly succumb to the action of benzene or benzole vapours than individuals of a less vigorous type. It will be readily understood that liability to poisoning is greater during hot days when the air is very stagnant. It should be borne in mind particularly that poisoning by benzole does not always mean that the patient becomes unconscious ; it is quite possible for a person working constantly in the vapours of benzole to become gradually poisoned, and failure in health will result after a time. Any suspected cases should be put under observation, and naturally taken off from work in the proximity of benzole.

Benzole is also responsible, among other of the light coal-tar distillates, for diseases coming under the heading of industrial dermatitis, and it should be noted here that petroleum distillates bring about similar troubles. The primary cause of this trouble is the removal of the natural grease from the skin by the light solvents. Cracking then occurs, sometimes very badly, and often eczematous growths appear round the cracks. Unless attention is given immediately one or other of these conditions arise ; bacterial poisoning will occur and intensify the condition of the disease. Employees should be cautioned not to use benzole or light coal tar oils for cleansing their hands, and should they have to work with this material they should keep their hands well greased with an antiseptic ointment, using as a base, lanoline. It goes without saying that it is very wise to send a case of this nature to a doctor should it show signs of becoming acute.

Pitch Cancer

This has been dealt with in Chapter XIX, page 333.

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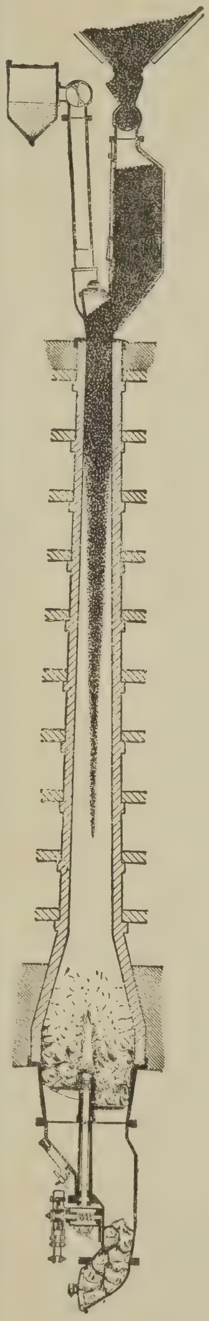

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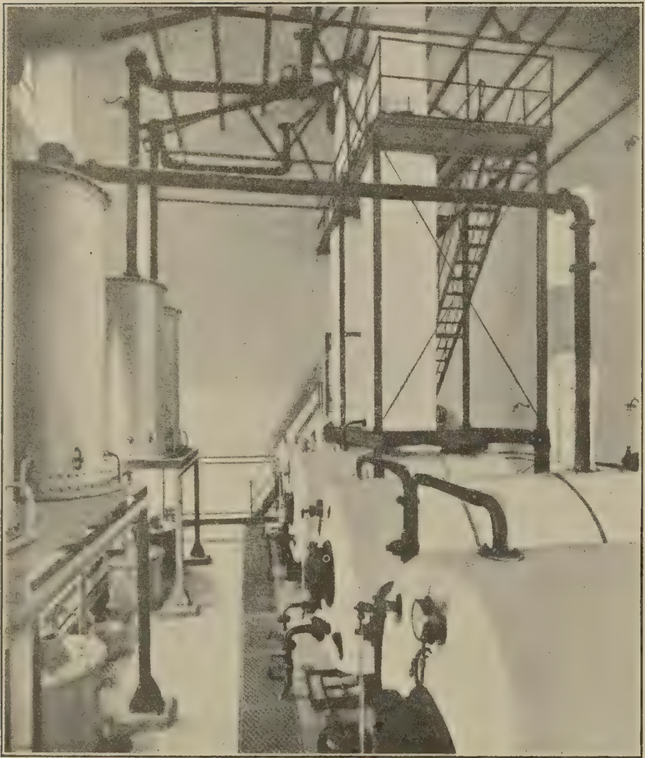

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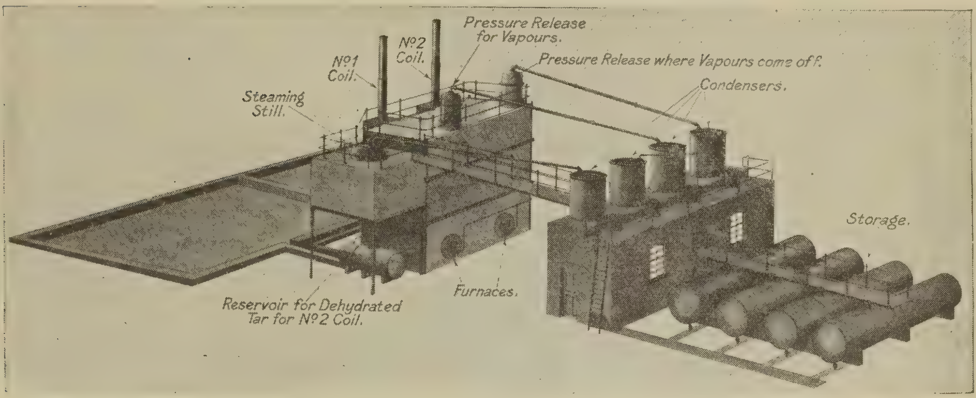
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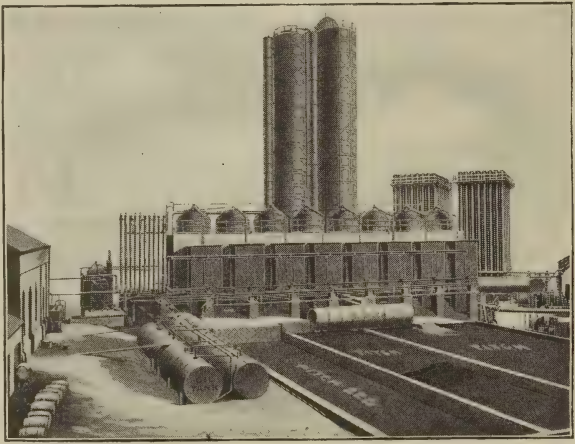

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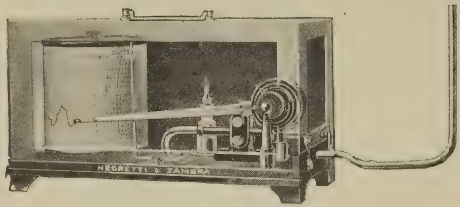

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